

**THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES**

Appellant(s): Shang et al.
Appl. No.: 10/688,843
Conf. No.: 9443
Filed: October 17, 2003
Title: HIGH IMPACT STRENGTH FILM AND NON-PVC CONTAINING
CONTAINER AND POUCH AND OVERPOUCH
Art Unit: 1794
Examiner: Marc A. Patterson
Docket No.: CPDI-5855 (112713-949)

Mail Stop Appeal Brief - Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

APPELLANTS' APPEAL BRIEF

Sir:

Appellants submit this Appeal Brief in support of the Notice of Appeal filed on October 26, 2007. This Appeal is taken from the Final Rejection in the Office Action dated October 4, 2007.

I. REAL PARTIES IN INTEREST

The real parties in interest for the above-identified patent application on Appeal are Baxter International Inc. and Baxter Healthcare S.A., by virtue of an Assignment recorded on March 9, 2006 at reel 017320, frames 0472-0475 in the United States Patent and Trademark Office.

II. RELATED APPEALS AND INTERFERENCES

Appellants' legal representative and the Assignees of the this patent application do not know of any prior or pending appeals, interferences or judicial proceedings that may be related to, directly affect or be directly affected by or have a bearing on the Board's decision with respect to the above-identified Appeal.

III. STATUS OF CLAIMS

Claims 1-17 are pending in this application. Claims 18-39 were previously withdrawn due to an election of species requirement dated March 22, 2006. Claims 41-66 were previously canceled. Claims 1-17 stand rejected. Therefore, Claims 1-17 are being appealed in this Brief. A copy of the appealed claims is included in the Claims Appendix.

IV. STATUS OF AMENDMENTS

A non-final Office Action was mailed on April 19, 2007. Appellants responded to the non-final Office Action on July 13, 2007, without amending the claims to overcome the rejections set forth in the non-final Office Action. A final Office Action maintaining the rejections was mailed on October 4, 2007. Appellants filed a Notice of Appeal on October 26, 2007. A copy of the non-final Office Action and final Office Action are attached as Exhibits A and B, respectively, in the Evidence Appendix.

V. SUMMARY OF CLAIMED SUBJECT MATTER

A summary of the claimed subject matter by way of reference to the specification and/or figures for each of the independent claims is provided as follows:

Independent Claim 1 is directed to a cross-link free monolayer film (page 2, lines 22-31; page 3, lines 1-2; page 8, lines 3-5; page 10, lines 12-27; Figure 4) comprising a polymer blend of a first component selected from the group consisting of 1) ethylene and α -olefin interpolymers having a density of less than about 0.915 g/cc, (2) ethylene and lower alkyl acrylate interpolymers, (3) ethylene and lower alkyl substituted alkyl acrylate interpolymers and (4) ionomers (page 7, line 25 to page 10, line 11; page 12, lines 4-17), the first component present in an amount by weight of the film from about 10% to about 50% (page 12, lines 1-3), the first component having a first melting point temperature determined by DSC (page 2, lines 22-31), a second component selected from the group consisting of propylene containing polymers and methyl pentene containing polymers (page 2, lines 22-31; page 12, line 18 to page 14, line 22), the second component being present in an amount by weight of the film from about 50% to about 90% (page 12, lines 18-20), the second component having a second melting point temperature determined by DSC (page 2, lines 22-31); and the film being capable of withstanding steam sterilization at a temperature from about 100°C to about 130°C (page 2, lines 22-31; page 18, lines 9-14).

Although specification citations are given in accordance with 37 C.F.R. §1.192(c), these reference numerals and citations are merely examples of support in the specification for the terms used in this section of the Brief. There is no intention to suggest in any way that the terms of the claims are limited to the examples in the specification. As demonstrated by the references numerals and citations, the claims are fully supported by the specification as required by law. However, it is improper under the law to read limitations from the specification into the claims. Pointing out specification support for the claim terminology in accordance with Rule 1.192(c) does not in any way limit the scope of the claims to those examples from which they find support. Nor does this exercise provide a mechanism for circumventing the law precluding reading limitations into the claims from the specification. In short, the references numerals and specification citations are not to be construed as claim limitations or in any way used to limit the scope of the claims.

VI. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

1. Claims 1-6 and 12-17 stand rejected under 35 U.S.C. §102(b) as anticipated by U.S. Patent Publication No. 2002/0115795 to Shang et al. (*Shang*). A copy of *Shang* is attached hereto as Exhibit C in the Evidence Appendix.
2. Claims 7-8 stand rejected under 35 U.S.C. §103(a) as being unpatentable over *Shang* in view of U.S. Patent No. 5,397,842 to Hamilton (*Hamilton*). A copy of *Hamilton* is attached hereto as Exhibit D in the Evidence Appendix.
3. Claims 9-11 stand rejected under 35 U.S.C. §103(a) as being unpatentable over *Shang* in view of U.S. Patent No. 6,346,308 to Cahill et al. (*Cahill*). A copy of *Cahill* is attached hereto as Exhibit E in the Evidence Appendix.

VII. ARGUMENT

A. LEGAL STANDARDS

1. Anticipation under 35 U.S.C. §102

Anticipation is a factual determination that “...requires the presence in a single prior art disclosure of each and every element of a claimed invention.” *Lewmar Marine, Inc. v. Barient, Inc.*, 3 U.S.P.Q.2d 1766 (Fed. Cir. 1987). Moreover, “[a] claim is anticipated only if each and every element as set forth in the claim is found, either expressly or inherently described, in a single prior art reference.” *Verdegaal Bros. v. Union Oil of California*, 2 U.S.P.Q.2d 1051, 1053 (Fed. Cir. 1987).

Federal Circuit decisions have repeatedly emphasized the notion that anticipation cannot be found where less than all elements of a claimed invention are set forth in a reference. *See, e.g. Transclean Corp. v. Bridgewood Services, Inc.*, 290 F.3d 1364 (Fed. Cir. 2002). In this regard, a reference disclosing “substantially the same thing” is not enough to anticipate. *Jamesbury Corp. v. Litton Indust. Prod., Inc.*, 756 F.2d 1556, 1560 (Fed. Cir. 1985). A reference must clearly disclose each and every limitation of the claimed invention before anticipation may be found.

2. Obviousness under 35 U.S.C. §103

The Federal Circuit has held that the legal basis for a determination of obviousness under 35 U.S.C. § 103 is:

whether the claimed invention as a whole would have been obvious to a person of ordinary skill in the art at the time the invention was made...The foundational facts for the prima facie case of obviousness are: (1) the scope and content of the prior art; (2) the difference between the prior art and the claimed invention; and (3) the level of ordinary skill in the art...Moreover, objective indicia such as commercial success and long felt need are relevant to the determination of obviousness...Thus, each obviousness determination rests on its own facts.

In re Mayne, 41 U.S.P.Q. 2d 1451, 1453 (Fed. Cir. 1997).

In making this determination, the Patent Office has the initial burden of proving a *prima facie* case of obviousness. *In re Rijckaert*, 9 F.3d 1531, 1532, 28 U.S.P.Q. 2d 1955, 1956 (Fed. Cir. 1993). This burden may only be overcome “by showing some objective teaching in the prior art or that knowledge generally available to one of ordinary skill in the art would lead that individual to combine the relevant teachings.” *In re Fine*, 837 F.2d 1071, 1074, 5 U.S.P.Q. 2d 1596, 1598 (Fed. Cir. 1988). “If the examination at the initial stage does not produce a *prima facie* case of unpatentability, then without more the applicant is entitled to grant of the patent.” *In re Oetiker*, 24 U.S.P.Q. 2d 1443, 1444 (Fed. Cir. 1992).

Moreover, the Patent Office must provide explicit reasons why the claimed invention is obvious in view of the prior art. The Supreme Court has emphasized that when formulating a rejection under 35 U.S.C. § 103(a) based upon a combination of prior art elements it remains necessary to identify the reason why a person of ordinary skill in the art would have combined the prior art elements in the manner claimed. *KSR v. Teleflex*, 127 S. Ct. 1727 (2007).

Of course, references must be considered as a whole and those portions teaching against or away from the claimed invention must be considered. *Bausch & Lomb, Inc. v. Barnes-Hind/Hydrocurve Inc.*, 796 F.2d 443 (Fed. Cir. 1986). “A prior art reference may be considered to teach away when a person of ordinary skill, upon reading the reference would be discouraged from following the path set out in the reference, or would be led in a direction divergent from the path that was taken by the Applicant.” *Monarch Knitting Mach. Corp. v. Fukuhara Indus. Trading Co., Ltd.*, 139 F.3d 1009 (Fed. Cir. 1998) (quoting *In re Gurley*, 27 F.3d 551 (Fed. Cir. 1994)).

B. THE CLAIMED INVENTION

There is one independent claim on appeal: Claim 1. Independent Claim 1 is generally directed to a cross-link free monolayer film comprising a polymer blend of a first component and a second component. The first component is selected from the group consisting of 1) ethylene and α -olefin interpolymers having a density of less than about 0.915 g/cc, (2) ethylene and lower alkyl acrylate interpolymers, (3) ethylene and lower alkyl substituted alkyl acrylate interpolymers and (4) ionomers. The first component is present in an amount from about 10% to about 50% by weight of the film. The first component has a first melting point temperature

determined by DSC. The second component is selected from the group consisting of propylene containing polymers and methyl pentene containing polymers. The second component is present in an amount from about 50% to about 90% by weight of the film and has a second melting point temperature determined by DSC. The film is capable of withstanding steam sterilization at a temperature from about 100°C to about 130°C.

C. THE REJECTION OF CLAIMS 1-6 AND 12-17 UNDER 35 U.S.C. §102(B) TO SHANG SHOULD BE REVERSED BECAUSE SHANG FAILS TO DISCLOSE EVERY ELEMENT OF THE CLAIMED INVENTION

Independent Claim 1 recites, in part, a cross-link free monolayer film comprising a polymer blend of a first component selected from the group consisting of 1) ethylene and α -olefin interpolymers having a density of less than about 0.915 g/cc, (2) ethylene and lower alkyl acrylate interpolymers, (3) ethylene and lower alkyl substituted alkyl acrylate interpolymers and (4) ionomers and a second component selected from the group consisting of propylene containing polymers and methyl pentene containing polymers. For example, the film does not require that any of its components be cross-linked or be exposed to cross-linking radiation. In contrast, Appellants respectfully submit that *Shang* is deficient with respect to the present claims.

Appellants have surprisingly found improved polymer blends for fabricating monolayer and multilayer films. The polymer blends for fabricating films have high impact strength and high barrier to water and gas transmission. Moreover, the films are capable of withstanding terminal steam sterilization without exposing the film to radiation or other cross-linking techniques. The claimed films can be suitable for fabricating primary containers and overpouches for containers used in medical and other applications. The claimed films can provide overpouch/container material that is functional over a wide range of temperatures and exhibits high impact strength after exposure to such temperatures.

The claimed films are also capable of being sealed using standard heat sealing techniques. For example, an adequate heat seal is formed when a fluid container, such as the one shown in FIG. 3 of the specification, is fabricated from the film by sealing peripheral edges to define a centrally disposed fluid chamber. The container can then be filled with an appropriate

fluid and subjected to a standard autoclave sterilization process. Adequate heat seals remain intact upon completion of the autoclave cycle.

Shang fails to disclose or suggest a number of elements of the claimed films. For example, *Shang* fails to disclose or suggest a cross-link free monolayer film comprising the polymer blend as required by Claim 1. Because the term “cross-link free” modifies the monolayer film and does not individually modify the first component or the second component, the proper claim interpretation is that the monolayer film is cross-link free. In other words, the claimed “cross-link free film” is a film, the entirety of which comprises no cross-linked component. In contrast, *Shang* discloses that its monolayer film is made from at least a cross-linked first component. See *Shang*, paragraph 24. The Examiner even admits same. See Office Action page 2.

Shang further teaches the following:

The present invention also provides other polymer blends suitable for fabricating a monolayer film, a multilayer film, a peel-seal film, a food or medical product container, a multichamber container, a multichamber peel seal container, an I.V. bag, a dialysis container, a nutritional-fluids container, and the like. The polymer blends have at least two components. The first component is a readily cross-linkable polymer and more preferably an ethylene-containing polymer. The second component is a non-readily cross-linkable polymer and more preferably a propylene-containing polymer. The blend is exposed to radiation to cross-link the first component but not the second component. The first component has a first melting point temperature determined by differential scanning calorimetry (DSC) and the second component has a second melting point temperature determined by DSC that is higher than the first melting point temperature. (See FIG. 7)

See *Shang*, paragraph 68 (emphasis added).

Accordingly, *Shang* explicitly discloses that its monolayer film has a cross-linked first component.

The Examiner asserts that *Shang's* film, which has a cross-linked first component and a non-cross-linked second component, teaches a partially cross-link free film and therefore anticipates the cross-link free film of the present claims. See Office Action, page 2, paragraph 2. Appellants respectfully submit that the Examiner is mischaracterizing *Shang's* film in an attempt to arrive at the present claims. For example, a partially cross-link free monolayer film does not anticipate a cross-link free monolayer film that contains no cross-linking portions anywhere within the film because each film comprises distinguishable physical structures and characteristics. The former film has cross-linked properties while the latter film does not.

Indeed, *Shang* specifically teaches that a cross-link comprises chemical linkages formed between different polymer molecules or between different segments of the same polymer molecule. Cross-linked polymers will show a significant increase in melt viscosity from a non-cross-linked version of the same polymer. See *Shang*, paragraph 69.

In contrast to *Shang*'s disclosure of a partially cross-linked monolayer film, Appellants' specification teaches that the claimed film does not require any of its components to be cross-linked or be exposed to cross-linking radiation. See, specification, page 3 lines 1-2. Thus, the recited element of "a cross-link free film" is a film that is not cross-linked or contains no cross-linked components anywhere within the film. To assert that *Shang*'s partially cross-linked film discloses the claimed cross-link free film is inconsistent with the meaning of "a cross-link free film" as set forth in the present application.

Shang also fails to disclose or suggest a two-component polymer blend having a first ethylene-based component being present in an amount of 10-50% by weight of the film and a second propylene/methyl pentene component present in an amount of 50-90% by weight of the film as required by Claim 1. Instead, *Shang* is primarily directed to a film made of a blend comprising a cross-linked first component being an ethylene-based component present in an amount of 55-99% by weight and a second component being present in an amount of 1-45% by weight. See *Shang*, paragraphs 38-39. As the weight percentages of the claimed first and second components are in direct contrast to the weight ranges disclosed for the first and second components of the *Shang*, *Shang* is deficient with respect to same.

In sum, *Shang* fails to disclose a number of elements of the claimed subject matter. Moreover, *Shang* fails to even recognize the advantages, benefits and/or properties of a cross-link free film in accordance with the present claims.

For at least the reasons identified above, *Shang* fails to disclose or even suggest every element of Claim 1, as well as Claims 2-6 and 12-17 that depend from Claim 1. Accordingly, Appellants respectfully submit that Claims 1-6 and 12-17 are novel, nonobvious and distinguishable from the cited reference and are in condition for allowance.

D. THE REJECTION OF CLAIMS 7-8 UNDER 35 U.S.C. §103(A) TO *SHANG* AND *HAMILTON* IS IMPROPER IN VIEW OF THE PATENTABILITY OF INDEPENDENT CLAIM 1

Claims 7-8 stand rejected under 35 U.S.C. §103(a) as being unpatentable over *Shang* and *Hamilton*. Appellants respectfully submit that the patentability of Claim 1 over *Shang* as discussed above also demonstrates that the obviousness rejection of Claims 7-8, which depend from Claim 1, is improper. In this regard, even with *Hamilton* as a reference, the cited art fails to teach or suggest the elements of Claims 7-8 in combination with the novel elements of Claim 1.

For example, *Shang* fails to disclose or suggest a number of elements required by Claim 1 as discussed previously. *Hamilton* fails to remedy the deficiencies of *Shang*. *Hamilton* is directed to a polymer blend composed of 1) a polyolefin and 2) a segmented copolymer. *Hamilton*, column 3, lines 33-62. *Hamilton*'s segmented copolymer is a polyolefin and vinyl aromatic copolymer. *Id.* Consequently, *Hamilton* fails to disclose or suggest cross-link free film comprising an ethylene-based first component and a propylene/methyl pentene second component as required by Claim 1. Moreover, the *Hamilton* blend may be cross-linked, further leading the skilled artisan away from the present claims. See *Hamilton*, column 3, lines 60-63 and column 5, lines 61-68.

Accordingly, Appellants respectfully submit that Claims 7-8 are novel, nonobvious and distinguishable from the cited references and are in condition for allowance.

E. THE REJECTION OF CLAIMS 9-11 UNDER 35 U.S.C. §103(A) TO *SHANG* AND *CAHILL* IS IMPROPER IN VIEW OF THE PATENTABILITY OF INDEPENDENT CLAIM 1

Claims 9-11 stand rejected under 35 U.S.C. §103(a) as being unpatentable over *Shang* and *Cahill*. Appellants respectfully submit that the patentability of Claim 1 over *Shang* as discussed above also demonstrates that the obviousness rejection of Claims 9-11, which depend from Claim 1, is improper. In this regard, even with *Cahill* as a reference, the cited art fails to teach or suggest the elements of Claims 9-11 in combination with the novel elements of Claim 1.

For example, *Shang* fails to disclose or suggest a number of elements required by Claim 1 as discussed previously. *Cahill* fails to remedy the deficiencies of *Shang*. *Cahill* is directed to

an oxygen barrier composition that may be used with polyolefin-based packaging. See *Cahill*, column 5, lines 30-40. *Cahill*, however, fails to disclose or suggest any cross-link free film comprising an ethylene-based first component present in an amount of 10-50% by weight of the blend and a propylene/methyl pentene based second component present in an amount of 50-99% by weight of the blend as required by Claim 1. *Cahill* along with *Shang* therefore fail to disclose or suggest the claimed subject matter.

Accordingly, Appellants respectfully submit that Claims 9-11 are novel, nonobvious and distinguishable from the cited references and are in condition for allowance.

VIII. CONCLUSION

Appellants respectfully submit that the Examiner has failed to establish anticipation under 35 U.S.C. §102 and a *prima facie* case of obviousness under 35 U.S.C. §103 with respect to the rejections of Claims 1-17. Accordingly, Appellants respectfully submit that the anticipation and obviousness rejections are erroneous in law and in fact and should therefore be reversed by this Board.

A check in the amount of \$510 is submitted herewith to cover the cost of the Appeal Brief. The Director is authorized to charge any additional fees that may be required, or to credit any overpayment to Deposit Account No. 02-1818. If such a withdrawal is made, please indicate the Attorney Docket No. 112713-949 on the account statement.

Respectfully submitted,

BELL, BOYD & LLOYD LLC

BY 

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Dated: December 20, 2007

CLAIMS APPENDIX
PENDING CLAIMS ON APPEAL OF
U.S. PATENT APPLICATION SERIAL NO. 10/688,843

1. A cross-link free monolayer film comprising:

a polymer blend of a first component selected from the group consisting of 1) ethylene and α -olefin interpolymers having a density of less than about 0.915 g/cc, (2) ethylene and lower alkyl acrylate interpolymers, (3) ethylene and lower alkyl substituted alkyl acrylate interpolymers and (4) ionomers, the first component present in an amount by weight of the film from about 10% to about 50%, the first component having a first melting point temperature determined by DSC, a second component selected from the group consisting of propylene containing polymers and methyl pentene containing polymers, the second component being present in an amount by weight of the film from about 50% to about 90%, the second component having a second melting point temperature determined by DSC; and the film being capable of withstanding steam sterilization at a temperature from about 100°C to about 130°C.

2. The film of claim 1, wherein the second melting point temperature is higher than the first melting point temperature.

3. The film of claim 1 wherein the ethylene containing polymer is obtained using a catalyst selected from the group consisting of: Ziegler-Natta and single-site.

4. The film of claim 1, wherein the ethylene containing polymer is selected from the group consisting of: ethylene homopolymers, and ethylene copolymers.

5. The film of claim 1, wherein the propylene containing polymer is selected from the group of propylene homopolymers and propylene copolymers.

6. The film of claim 5, wherein the propylene containing polymer is obtained using a catalyst selected from the group consisting of: Ziegler-Natta and single-site.

7. The film of claim 1, wherein the propylene containing polymer is a high melt strength polymer.

8. The film of claim 7, wherein the high melt strength propylene containing polymer is selected from the propylene containing propylene made from electron beam process and reactor made process.

9. The film of claim 1 further comprising an oxygen scavenger.

10. The film of claim 9, wherein the oxygen scavenger is an oxidizable polydiene.

11. The film of claim 9, wherein the oxygen scavenger is an oxidizable polyether.

12. The film of claim 1, wherein the film is prepared by a process selected from the group consisting of extrusion, calendering, blown film extrusion and blown molding.

13. The film of claim 1, wherein the film is capable of being fabricated into a liquid filled container wherein the container has sufficient impact strength to resist rupturing when dropped from 8 feet.

14. The film of claim 1, wherein the film is capable of being fabricated into a liquid filled container wherein the container is capable of being terminally sterilized by exposure to steam at 121° C. for one hour.

15. The film of claim 1, wherein the film is capable of being sterilized by steam sterilization exposure to radiation and exposure to ethylene oxide.

16. The film of claim 1, wherein the film is capable of forming a peel seal to form a multiple chambered container.

17. The film of claim 16, wherein the film is further capable of forming a permanent seal to form a multiple chambered container

EVIDENCE APPENDIX

EXHIBIT A: Non-final Office Action dated April 19, 2007

EXHIBIT B: Final Office Action dated October 4, 2007

EXHIBIT C: U.S. Patent Publication No. 2002/0115795 to Shang et al. (*Shang*), cited by the Examiner in the Office Action dated October 4, 2007

EXHIBIT D: U.S. Patent No. 5,397,842 to Hamilton (*Hamilton*), cited by the Examiner in the Office Action dated October 4, 2007

EXHIBIT E: U.S. Patent No. 6,346,308 to Cahill et al. (*Cahill*), cited by the Examiner in the Office Action dated October 4, 2007

RELATED PROCEEDINGS APPENDIX

None

EXHIBIT A



UNITED STATES PATENT AND TRADEMARK OFFICE

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/688,843	10/17/2003	Sherwin Shang	DI-5855 US	9443
29200 7590 04/19/2007 BAXTER HEALTHCARE CORPORATION 1 BAXTER PARKWAY DF2-2E DEERFIELD, IL 60015			EXAMINER PATTERSON, MARC A	
			ART UNIT	PAPER NUMBER
			1772 Date: 7-19-07	
SHORTENED STATUTORY PERIOD OF RESPONSE	MAIL DATE	DELIVERY MODE		
3 MONTHS	04/19/2007	PAPER		

Please find below and/or attached an Office communication concerning this application or proceeding.

If NO period for reply is specified above, the maximum statutory period will apply and will expire 6 MONTHS from the mailing date of this communication.

RECEIVED
 BELL, BOYD & LLOYD
 INTELLECTUAL PROPERTY DOCKET

APR 30 2007
 ATTY: AMB-TJB
 DOCKET #: 112713-

0949

Office Action Summary	Application No.	Applicant(s)	
	10/688,843	SHANG ET AL.	
	Examiner	Art Unit	
	Marc A. Patterson	1772	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☒ Responsive to communication(s) filed on 02 February 2007.
- 2a) ☐ This action is FINAL. 2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

- 4) ☒ Claim(s) 1-40 is/are pending in the application.
- 4a) Of the above claim(s) _____ is/are withdrawn from consideration.
- 5) ☐ Claim(s) _____ is/are allowed.
- 6) ☒ Claim(s) 1-40 is/are rejected.
- 7) ☐ Claim(s) _____ is/are objected to.
- 8) ☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on _____ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

- 12) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All b) ☐ Some * c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
 2. ☐ Certified copies of the priority documents have been received in Application No. _____.
 3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

- | | |
|--|---|
| 1) <input type="checkbox"/> Notice of References Cited (PTO-892) | 4) <input type="checkbox"/> Interview Summary (PTO-413) |
| 2) <input type="checkbox"/> Notice of Draftsperson's Patent Drawing Review (PTO-948) | Paper No(s)/Mail Date, _____ |
| 3) <input type="checkbox"/> Information Disclosure Statement(s) (PTO/SB/08) | 5) <input type="checkbox"/> Notice of Informal Patent Application |
| Paper No(s)/Mail Date _____ | 6) <input type="checkbox"/> Other: _____ |

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Art Unit: 1772

Page 2

DETAILED ACTION

NEW REJECTIONS

Claim Rejections - 35 USC § 102

1. The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

A person shall be entitled to a patent unless –

(b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

2. Claims 1 – 6 and 12 – 17 are rejected under 35 U.S.C. 102(b) as being anticipated by Shang et al (U.S. Patent Publication No. 2002/0115795).

With regard to Claims 1 – 2 and 14, Shang et al disclose a monolayer film (paragraph 0038) comprising a blend of a first component of an ethylene – lower alkyl acrylate interpolymers (paragraph 0038) present in an amount of 50% by weight of the film (paragraph 0024) and a second component of a propylene containing polymer (paragraph 0039) present in an amount of 50% by weight of the film (paragraph 0024) and the film capable of withstanding steam sterilization at 121 degrees Celsius (therefore terminal sterilization by exposure to steam at 121 degrees Celsius for one hour; paragraph 0004) and the first and second components having melting point temperatures determined by DSC, and the second melting point temperature is higher than the first melting point temperature (paragraph 0068); a portion of the first component is crosslinked and the second component is free of crosslinking (paragraph 0024) and the film is therefore partially crosslink free.

With regard to Claims 3 and 6, the ethylene containing polymer is obtained using a single site catalyst (paragraph 0042).

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With regard to Claim 4, the ethylene containing polymer is a copolymer (paragraph 0073).

With regard to Claim 5, the propylene containing polymer is a copolymer (paragraph 0076).

With regard to Claim 12, the film is prepared by extrusion (paragraph 0085); however, the claimed aspect of the film being prepared by extrusion is a method limitation, rather than a structural limitation, and is therefore given little patentable weight.

With regard to Claims 13 and 15, the blend disclosed by Shang et al has a composition which is identical to the claimed invention, as stated above, and is capable of being fabricated into a liquid filled container (medical fluid container; paragraph 0004); the claimed aspects of the container having sufficient impact strength to resist rupturing when dropped from 8 feet and being capable of being sterilized by exposure to radiation are therefore inherent to Shang et al.

With regard to Claim 16, the film is capable of forming a peel seal to form a multiple chambered container (dual chambered container; paragraph 0100).

With regard to Claim 17, the film is capable of forming a permanent seal (paragraph 0083), therefore to form a multiple chambered container.

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Claim Rejections - 35 USC § 103

3. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

4. Claims 7 – 8 are rejected under 35 U.S.C. 103(a) as being unpatentable over Shang et al (U.S. Patent Publication No. 2002/0115795) in view of Hamilton et al (U.S. Patent No. 5,397,842).

Shang et al discloses a container comprising a propylene containing polymer as discussed above. With regard to Claims 7 – 8, Shang et al fail to disclose a propylene container comprising a high melt strength polymer.

Hamilton et al teach a container (column 3, line 68) comprising a propylene polymer that is a high melt strength polymer (Abstract) for the purpose of obtaining a container that is resistant to sag (column 1, lines 10 – 13). One of ordinary skill in the art would therefore have recognized the advantage of providing for the high melt strength polymer of Hamilton et al in Shang et al, which comprises a container, depending on the desired resistance to sag of the end product.

It therefore would have been obvious for one of ordinary skill in the art at the time Applicant's invention was made to have provided for a propylene container comprising a high melt strength polymer in Shang et al in order to obtain a container that is resistant to sag as taught by Hamilton et al.

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5. Claims 9 – 11 are rejected under 35 U.S.C. 103(a) as being unpatentable over Shang et al (U.S. Patent Publication No. 2002/0115795) in view of Cahill et al (U.S. Patent No. 6,346,308).

Shang et al disclose a polymer as discussed above. With regard to Claims 9 – 11, Shang et al fail to disclose a polymer comprising an oxygen scavenger comprising oxidizable polyether and polydiene.

Cahill et al teach a polymer comprising oxygen scavenger comprising oxidizable polyether or polydiene for the purpose of obtaining a polymer having an extended shelf life (polybutadiene; column 4, lines 18 – 36). One of ordinary skill in the art would therefore have recognized the advantage of providing for the oxygen scavenger of Cahill et al in Shang et al, which comprises a polymer, depending on the desired shelf life of the end product.

It therefore would have been obvious for one of ordinary skill in the art at the time Applicant's invention was made to have provided for a polymer comprising an oxygen scavenger comprising oxidizable polyether and polydiene in Shang et al in order to obtain a polymer having an extended shelf life as taught by Cahill et al

ANSWERS TO APPLICANT'S ARGUMENTS

6. Applicant's arguments regarding the 35 U.S.C. 102(b) rejection of Claims 1 – 6 and 12 – 17 as being anticipated by Shang et al (U.S. Patent Publication No. 2002/0115795), 35 U.S.C. 103(a) rejection of Claims 7 – 8 as being unpatentable over Shang et al (U.S. Patent Publication No. 2002/0115795) in view of Hamilton et al (U.S. Patent No. 5,397,842) and 35 U.S.C. 103(a) rejection of Claims 9 – 11 as being unpatentable over Shang et al (U.S. Patent Publication No. 2002/0115795) in view of Cahill et al (U.S. Patent No. 6,346,308), of record in the previous

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Action, have been carefully considered but have not been found to be persuasive for the reasons set forth below.

Applicant argues, on page 8 of the remarks dated February 2, 2007 that Shang et al do not disclose a film that is crosslink free.

However, as stated above, a portion of the first component disclosed by Shang et al is crosslinked and the second component is free of crosslinking, and the film disclosed by Shang et al is therefore partially crosslink free.

7. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Marc A Patterson whose telephone number is 571-272-1497.

The examiner can normally be reached on Mon - Fri 8:30 AM - 5:00 PM.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Harold Pyon can be reached on 571-272-1498. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

Marc A. Patterson 4/16/07
Marc A. Patterson, PhD.
Primary Examiner
Art Unit 1772

EXHIBIT B



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
 United States Patent and Trademark Office
 Address: COMMISSIONER FOR PATENTS
 P.O. Box 1450
 Alexandria, Virginia 22313-1450
 www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/688,843	10/17/2003	Sherwin Shang	DI-5855 US	9443

29200 7590 10/04/2007
 BAXTER HEALTHCARE CORPORATION
 1 BAXTER PARKWAY
 DF2-2E
 DEERFIELD, IL 60015

EXAMINER

PATTERSON, MARC A

ART UNIT	PAPER NUMBER
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1794

MAIL DATE	DELIVERY MODE
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10/04/2007

PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

RECEIVED

OCT 18 2007

Corporate Patent Administration

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 BELL, BOYD & LLOYD
 INTELLECTUAL PROPERTY DOCKET

OCT 18 2007

ATTY: — RMB-myb
 DOCKE. — 112713—

949

Office Action Summary**Application No.**

10/688,843

Applicant(s)

SHANG ET AL.

Examiner

Marc A. Patterson

Art Unit

1772

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --**Period for Reply**

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☒ Responsive to communication(s) filed on 13 July 2007.
- 2a) ☒ This action is FINAL. 2b) ☐ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

- 4) ☒ Claim(s) 1-17 is/are pending in the application.
- 4a) Of the above claim(s) _____ is/are withdrawn from consideration.
- 5) ☐ Claim(s) _____ is/are allowed.
- 6) ☒ Claim(s) 1-17 is/are rejected.
- 7) ☐ Claim(s) _____ is/are objected to.
- 8) ☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on _____ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

- 12) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All b) ☐ Some * c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
2. ☐ Certified copies of the priority documents have been received in Application No. _____.
3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

- 1) ☐ Notice of References Cited (PTO-892)
- 2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
- 3) ☐ Information Disclosure Statement(s) (PTO/SB/08)
Paper No(s)/Mail Date _____.
- 4) ☐ Interview Summary (PTO-413)
Paper No(s)/Mail Date. _____.
- 5) ☐ Notice of Informal Patent Application
- 6) ☐ Other: _____.

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DETAILED ACTION

NEW REJECTIONS

Claim Rejections - 35 USC § 102

1. The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

A person shall be entitled to a patent unless –

(b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

2. Claims 1 – 6 and 12 – 17 are rejected under 35 U.S.C. 102(b) as being anticipated by Shang et al (U.S. Patent Publication No. 2002/0115795).

With regard to Claims 1 – 2 and 14, Shang et al disclose a monolayer film (paragraph 0068) comprising a blend of a first component of an ethylene polymer (paragraph 0073) and a propylene – containing polymer (paragraph 0076) each present in an amount of 50% by weight of the film (paragraph 0074); the ethylene polymer is a polymer ‘set forth above’ (paragraph 0073) which is ethylene – lower alkyl acrylate interpolymer (paragraph 0038); the film is capable of withstanding steam sterilization at 121 degrees Celsius (therefore terminal sterilization by exposure to steam at 121 degrees Celsius for one hour; paragraph 0004) and the first and second components having melting point temperatures determined by DSC, and the second melting point temperature is higher than the first melting point temperature (paragraph 0068); a portion of the first component is crosslinked and the second component is free of crosslinking (paragraph 0024) and the film is therefore partially crosslink free.

With regard to Claims 3 and 6, the ethylene containing polymer is obtained using a single site catalyst (paragraph 0042).

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With regard to Claim 4, the ethylene containing polymer is a copolymer (paragraph 0073).

With regard to Claim 5, the propylene containing polymer is a copolymer (paragraph 0076).

With regard to Claim 12, the film is prepared by extrusion (paragraph 0085); however, the claimed aspect of the film being prepared by extrusion is a method limitation, rather than a structural limitation, and is therefore given little patentable weight.

With regard to Claims 13 and 15, the blend disclosed by Shang et al has a composition which is identical to the claimed invention, as stated above, and is capable of being fabricated into a liquid filled container (medical fluid container; paragraph 0004); the claimed aspects of the container having sufficient impact strength to resist rupturing when dropped from 8 feet and being capable of being sterilized by exposure to radiation are therefore inherent to Shang et al.

With regard to Claim 16, the film is capable of forming a peel seal to form a multiple chambered container (dual chambered container; paragraph 0100).

With regard to Claim 17, the film is capable of forming a permanent seal (paragraph 0083), therefore to form a multiple chambered container.

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Claim Rejections - 35 USC § 103

3. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

4. Claims 7 – 8 are rejected under 35 U.S.C. 103(a) as being unpatentable over Shang et al (U.S. Patent Publication No. 2002/0115795) in view of Hamilton et al (U.S. Patent No. 5,397,842).

Shang et al discloses a container comprising a propylene containing polymer as discussed above. With regard to Claims 7 – 8, Shang et al fail to disclose a propylene container comprising a high melt strength polymer.

Hamilton et al teach a container (column 3, line 68) comprising a propylene polymer that is a high melt strength polymer (Abstract) for the purpose of obtaining a container that is resistant to sag (column 1, lines 10 – 13). One of ordinary skill in the art would therefore have recognized the advantage of providing for the high melt strength polymer of Hamilton et al in Shang et al, which comprises a container, depending on the desired resistance to sag of the end product.

It therefore would have been obvious for one of ordinary skill in the art at the time Applicant's invention was made to have provided for a propylene container comprising a high melt strength polymer in Shang et al in order to obtain a container that is resistant to sag as taught by Hamilton et al.

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5. Claims 9 – 11 are rejected under 35 U.S.C. 103(a) as being unpatentable over Shang et al (U.S. Patent Publication No. 2002/0115795) in view of Cahill et al (U.S. Patent No. 6,346,308).

Shang et al disclose a polymer as discussed above. With regard to Claims 9 – 11, Shang et al fail to disclose a polymer comprising an oxygen scavenger comprising oxidizable polyether and polydiene.

Cahill et al teach a polymer comprising oxygen scavenger comprising oxidizable polyether or polydiene for the purpose of obtaining a polymer having an extended shelf life (polybutadiene; column 4, lines 18 – 36). One of ordinary skill in the art would therefore have recognized the advantage of providing for the oxygen scavenger of Cahill et al in Shang et al, which comprises a polymer, depending on the desired shelf life of the end product.

It therefore would have been obvious for one of ordinary skill in the art at the time Applicant's invention was made to have provided for a polymer comprising an oxygen scavenger comprising oxidizable polyether and polydiene in Shang et al in order to obtain a polymer having an extended shelf life as taught by Cahill et al.

ANSWERS TO APPLICANT'S ARGUMENTS

5. Applicant's arguments regarding the 35 U.S.C. 102(b) rejection of Claims 1 – 6 and 12 – 17 as being anticipated by Shang et al (U.S. Patent Publication No. 2002/0115795), 35 U.S.C. 103(a) rejection of Claims 7 – 8 as being unpatentable over Shang et al (U.S. Patent Publication No. 2002/0115795) in view of Hamilton et al (U.S. Patent No. 5,397,842) and 35 U.S.C. 103(a) rejection of Claims 9 – 11 as being unpatentable over Shang et al (U.S. Patent Publication No.

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2002/0115795) in view of Cahill et al (U.S. Patent No. 6,346,308), of record in the previous Action, have been carefully considered but have not been found to be persuasive for the reasons set forth below.

Applicant argues, on page 2 of the remarks dated July 13, 2007, that Shang et al fail to disclose a crosslink – free film.

However, as stated on page 2 of the previous Action, a crosslink – free film is disclosed by Shang et al.

Applicant also argues, on page 3, that Shang et al fail to disclose a first component and second component, each of which is 50% by weight of the blend.

However, as stated above, Shang et al disclose a first component and second component, each of which is 50% by weight of the blend.

Applicant also argues, on page 4, that Hamilton and Cahill et al fail to disclose a crosslink – free film.

However, as stated above, a crosslink – free film is disclosed by Shang et al.

6. Applicant's amendment necessitated the new ground(s) of rejection presented in this Office action. Accordingly, **THIS ACTION IS MADE FINAL**. See MPEP § 706.07(a). Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire **THREE MONTHS** from the mailing date of this action. In the event a first reply is filed within **TWO MONTHS** of the mailing date of this final action and the advisory action is not mailed until after the end of the **THREE-MONTH** shortened statutory period, then the shortened statutory period

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will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the date of this final action.

7. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Marc A Patterson whose telephone number is 571-272-1497. The examiner can normally be reached on Mon - Fri 8:30 AM - 5:00 PM.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Harold Pyon can be reached on 571-272-1498. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

Marc Patterson 10/1/07
Marc A. Patterson, PhD.
Primary Examiner
Art Unit 1772

EXHIBIT C

(19) **United States**(12) **Patent Application Publication** (10) **Pub. No.: US 2002/0115795 A1****Shang et al.**(43) **Pub. Date: Aug. 22, 2002**

(54) **AUTOCLAVABLE, NON-ADHERENT, HEAT SEALABLE POLYMER FILMS FOR FABRICATING MONOLAYER AND MULTIPLE LAYERED FILMS AND CONTAINERS**

Related U.S. Application Data

(63) Continuation-in-part of application No. 09/526,357, filed on Mar. 16, 2000.

Publication Classification

(51) **Int. Cl.⁷** **C08F 8/00**
(52) **U.S. Cl.** **525/192; 525/240**

(76) **Inventors:** Sherwin Shang, Vernon Hills, IL (US);
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Michael Becker, Chicago, IL (US);
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(21) **Appl. No.:** **09/917,136**

(22) **Filed:** **Jul. 27, 2001**

(57) **ABSTRACT**

The present invention provides polymer blends having a first component of a polymeric material capable of being cross-linked and selected from the group consisting of an ethylene containing polymer, the first component present in an amount by weight of the blend from about 50% to about 95%, the first component having a first melting point temperature determined by DSC; and a second component of a non-readily cross-linkable polymeric material and selected from the group consisting of propylene containing polymers and methyl pentene containing polymers, the second component being present in an amount by weight of the blend from about 50% to about 5%, the second component having a second melting point temperature determined by DSC; and a portion of the first component being cross-linked and the second component is essentially free of cross-linking.

FIG. 1

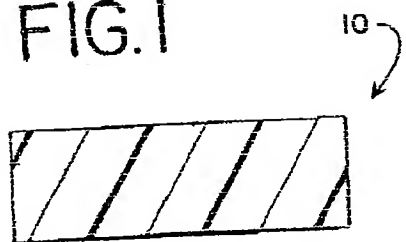


FIG. 2

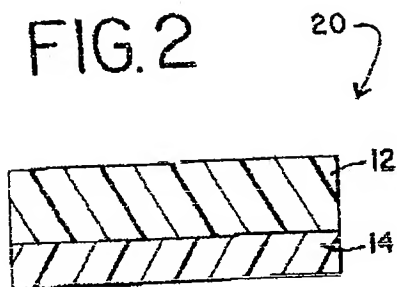
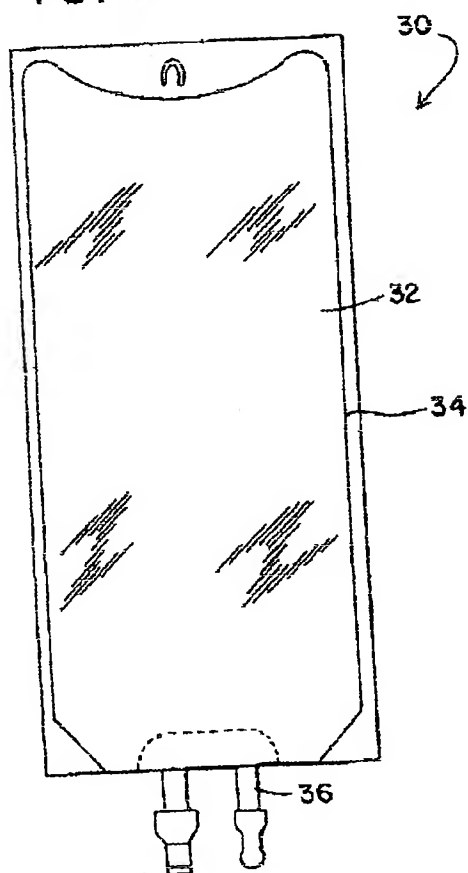


FIG. 3



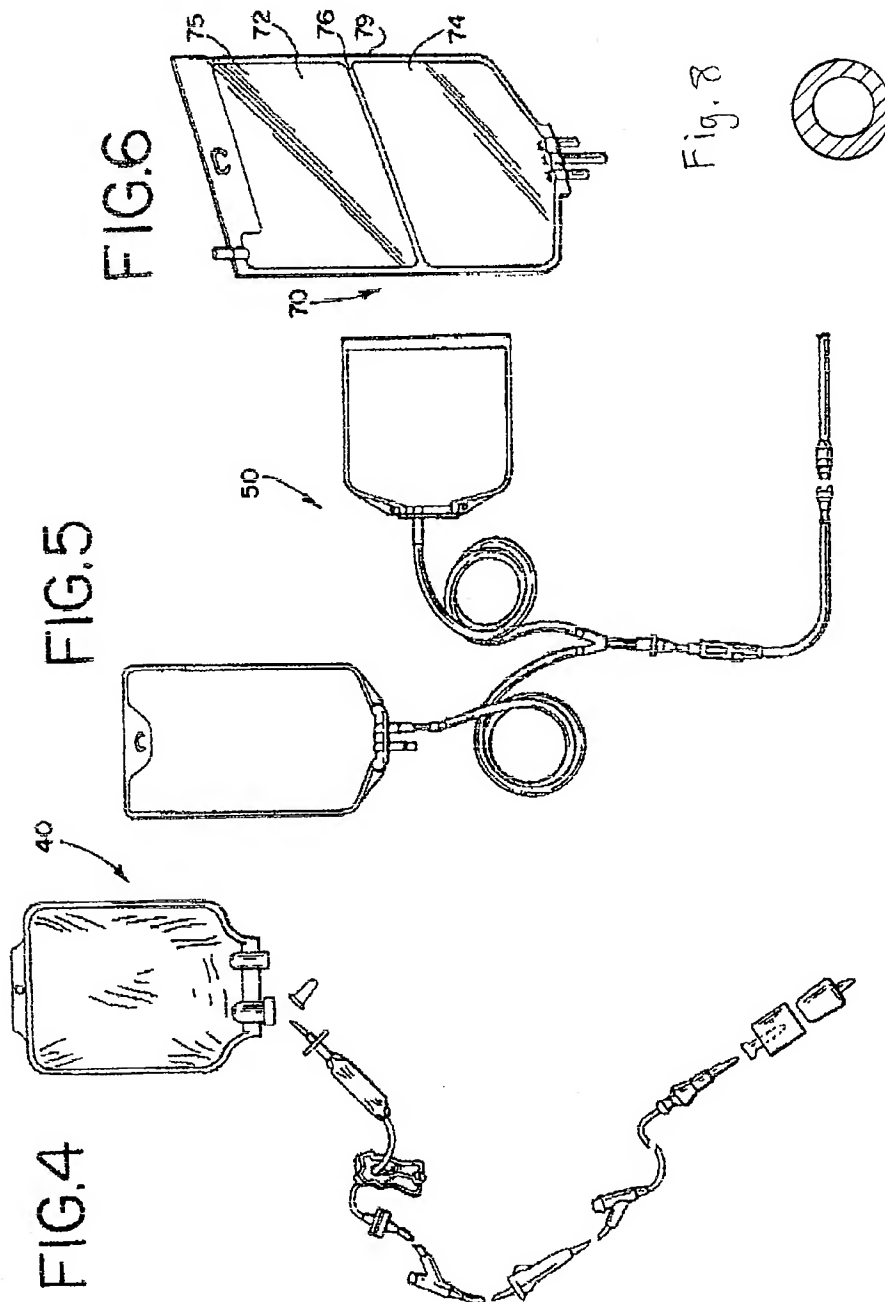


Fig. 7

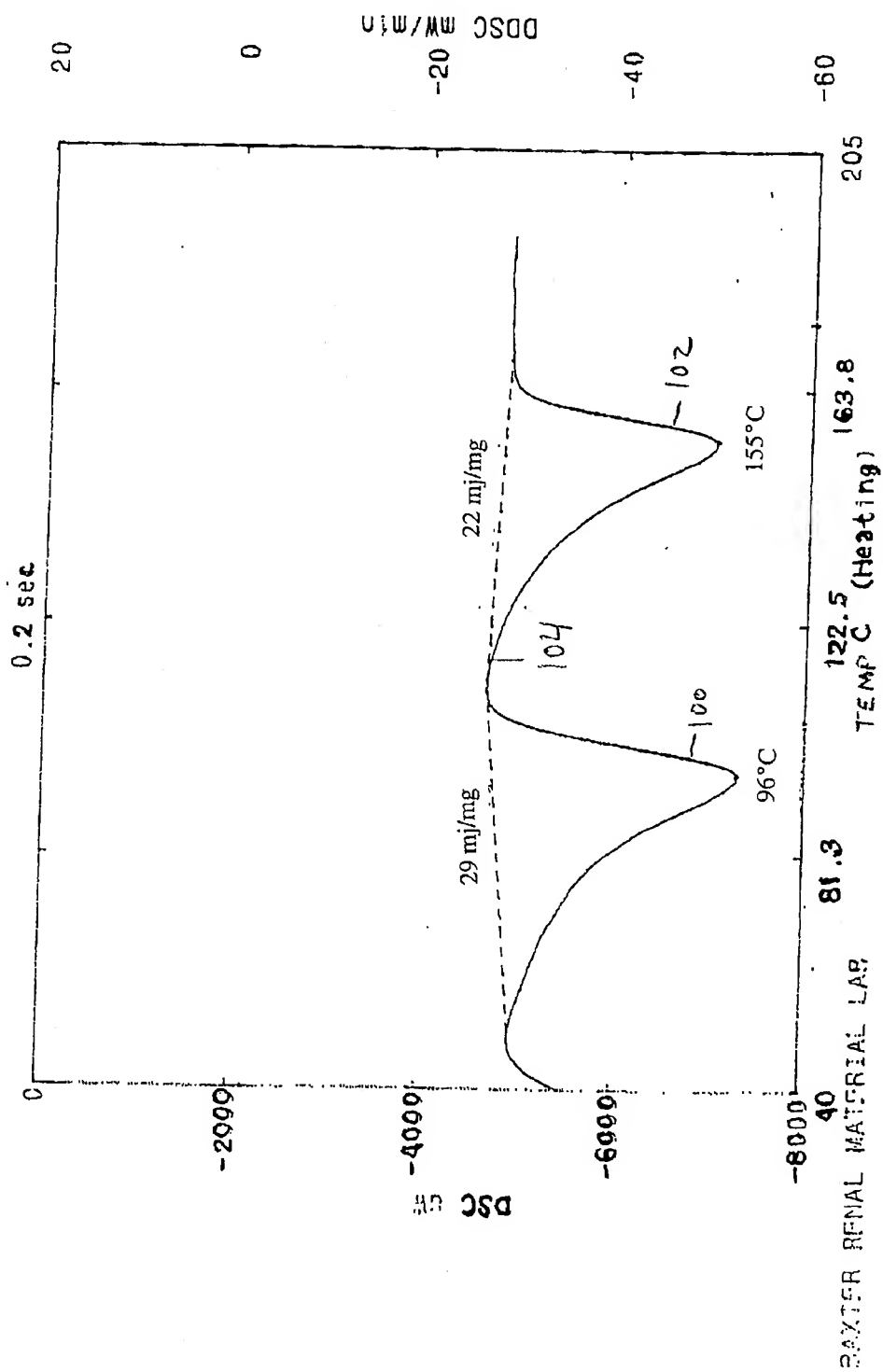
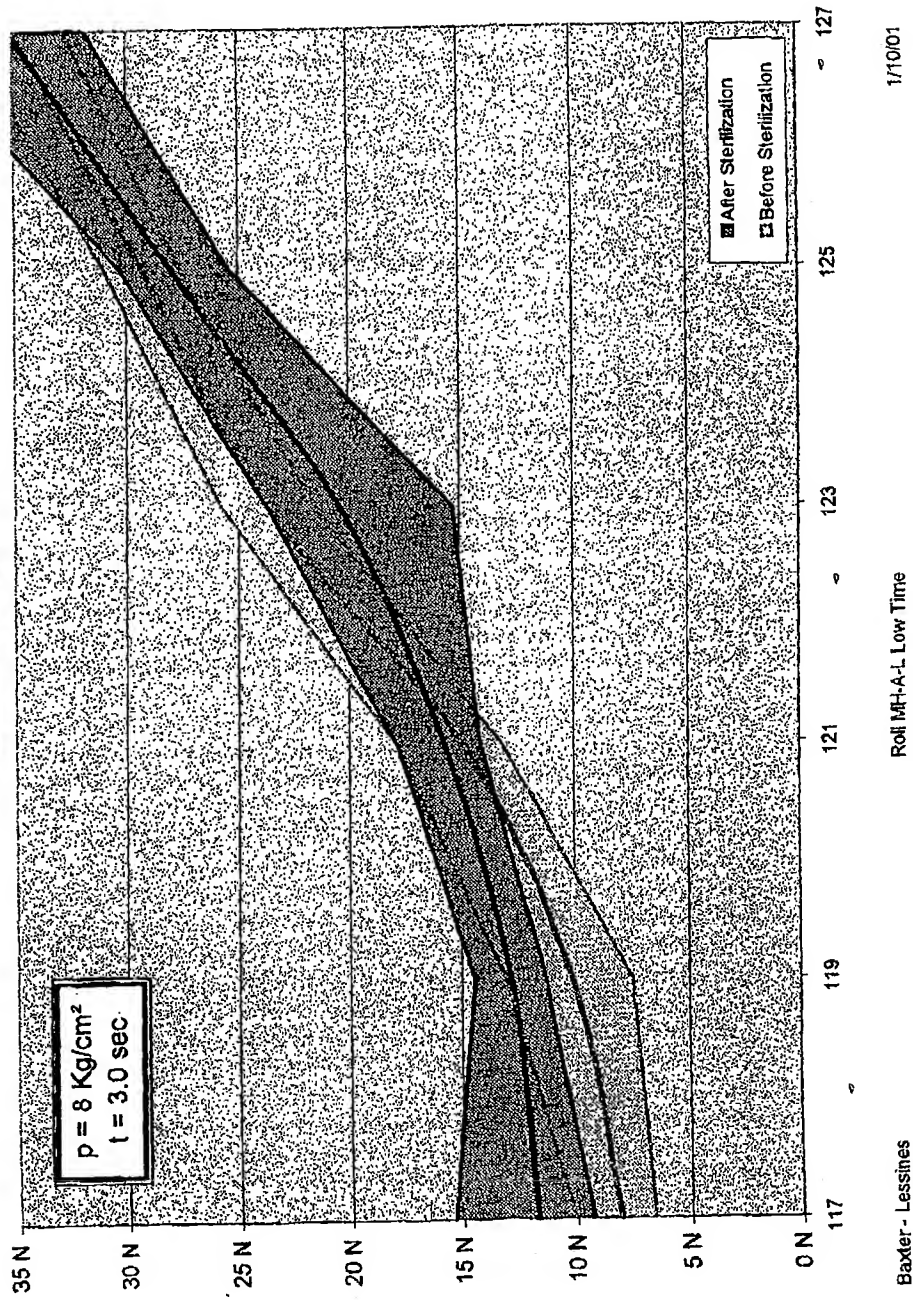


Fig 9
E-Beam Sheeting
Seal Force Versus Sealing Temperature

Roll MH #A-L



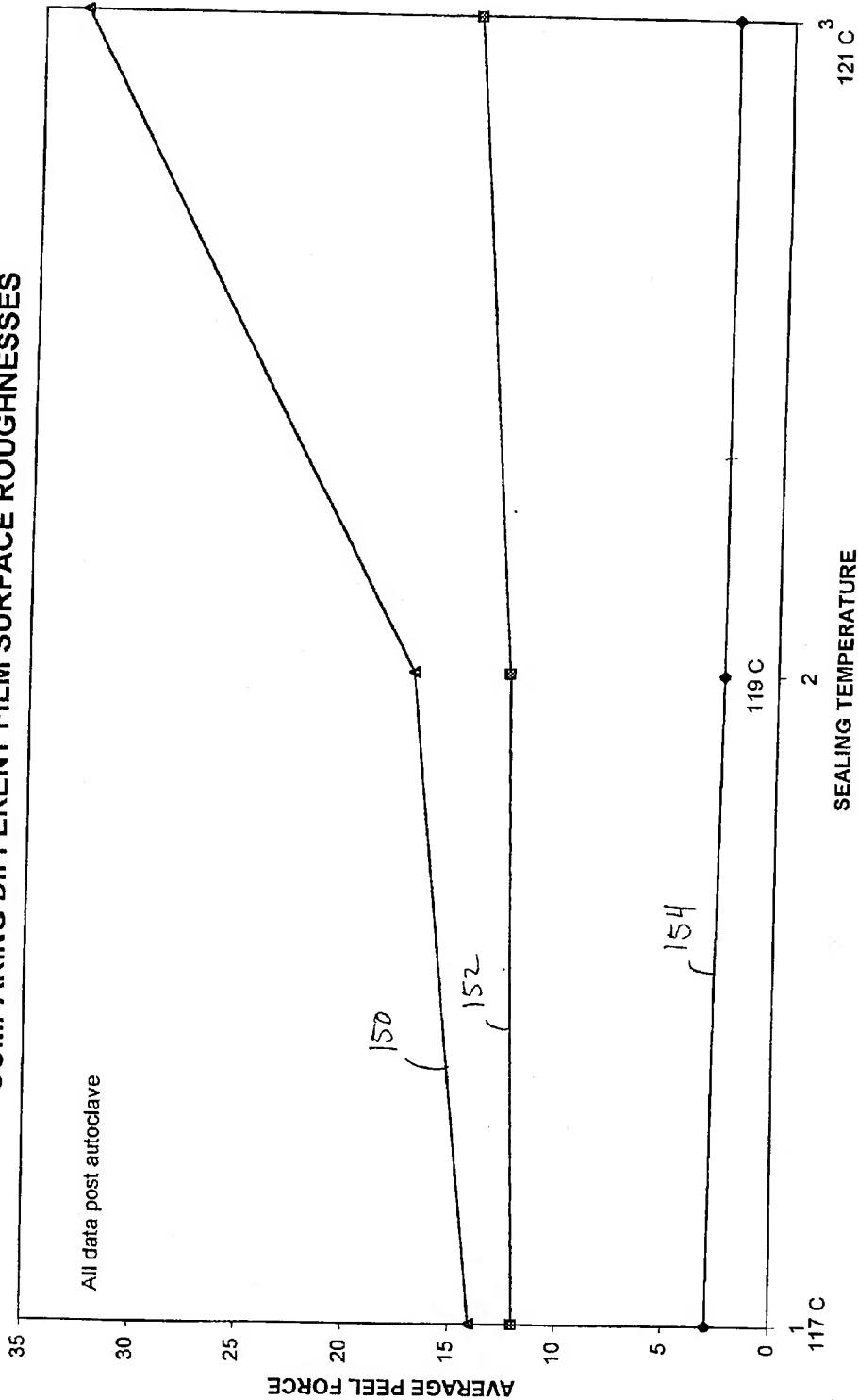
Baxter - Lessines

Roll MH-A-L Low Time

1/10/01

Fig. 10

PEEL SEAL FORCE vs. TEMPERATURE
COMPARING DIFFERENT FILM SURFACE ROUGHNESSES



**AUTOCLAVABLE, NON-ADHERENT, HEAT
SEALABLE POLYMER FILMS FOR FABRICATING
MONOLAYER AND MULTIPLE LAYERED FILMS
AND CONTAINERS**

**CROSS-REFERENCE TO RELATED
APPLICATIONS**

[0001] This is being filed as a Continuation-In-Part application of Ser. No. 09/526,357 filed on Mar. 16, 2000, which is incorporated

FEDERALLY SPONSORED RESEARCH

[0002] Not Applicable.

BACKGROUND OF THE INVENTION

TECHNICAL FIELD

[0003] The present invention relates generally to polymer blends for fabricating films and more particularly films that have low distortion and are non-adherent upon steam sterilization, are heat sealable and are suitable for fabricating into flexible medical containers.

[0004] In the medical field, where beneficial agents are collected, processed and stored in containers, transported, and ultimately delivered through tubes by infusion to patients to achieve therapeutic effects, materials which are used to fabricate the containers must have a unique combination of properties. For example, visual inspection of solutions for particulate contamination requires an optically transparent container. The material which forms the wall must be sufficiently flexible to infuse a solution by collapsing the container walls, without introducing air into the container. The material must maintain its flexibility and toughness over a wide range of temperatures. The material must maintain its flexibility and toughness at low temperatures because some solutions, for example, certain premixed drug solutions, are stored and transported in containers at temperatures such as -25°C . to -30°C . to minimize the drug degradation. The material must also be functional and resist distortion at high temperatures to withstand the heat of steam sterilization; a process which most medical fluid containers and nutritional products are subjected to prior to shipment. The sterilization process usually includes exposing the container to steam at temperatures typically 121°C . and at elevated pressures.

[0005] For ease of manufacture into useful articles, it is desirable that the material be sealable using heat sealing techniques. The material therefore must maintain sufficient thermoplastic properties to melt upon heating.

[0006] A further requirement is to minimize the environmental impact upon the disposal of the article fabricated from the material after its intended use. For those articles that are disposed of in landfills, it is desirable to minimize or avoid the incorporation of low molecular weight leachable components to construct the article. Further benefits are realized by using a material that allows thermal reprocessing of scrap material produced during manufacturing.

[0007] For those containers that are disposed of through incineration to minimize biological hazards, it is desirable to use a material that minimizes or eliminates the formation of environmentally undesirable and corrosive inorganic acids.

It is also desirable that the material be free from or have a low content of low molecular weight additives such as plasticizers, stabilizers and the like which could be released into the medications or biological fluids.

[0008] Due to its ability to meet a wide variety of functional requirements, flexible polyvinyl chloride (PVC) has frequently been the material of choice for medical bag applications. PVC also offers the distinct advantage of being one of the most cost-effective materials for constructing devices that meet the above requirements. However, PVC has a number of disadvantages in the marketplace. These disadvantages include incompatibility of PVC compounds with certain drugs, concerns regarding chlorine content and its effects on the environment and a growing negative market perception of PVC in general. Thus, many materials have been devised to replace PVC. However, most alternate materials are too expensive to implement and still do not meet all of the above requirements.

[0009] Polyolefins and polyolefin alloys have been developed which meet many of the requirements of medical containers and tubing, without the disadvantages associated with PVC. Polyolefins typically are compatible with medical applications because they have relatively low extractability to fluids. Most polyolefins are environmentally sound as they do not generate harmful degradants upon incineration, and are suitable for thermoplastic recycling. Many polyolefins are cost effective materials that may provide an economic alternative to PVC. However, there are many hurdles to overcome to replace all the favorable attributes of PVC with a polyolefin.

[0010] For example, problems have been encountered in using certain polyolefins to fabricate medical tubing. Such tubing has been found to have poor surface characteristics so that it is readily susceptible to cutting, shredding or scoring when clamping the tubing using a slide clamp. Also, certain polyolefins that have favorable modulus attributes, such as ultra-low density polyethylenes, have melting point temperatures below that reached during an autoclave process.

[0011] It is well known that cross-linking by chemical agents or by high energy ionizing radiation increases heat resistance of the polymer matrix. The chemical cross-links are covalent bonds across separate polymer chains that greatly retard the tendency to deform and flow at high temperatures—even above the melting point of the polymer. For example, U.S. Pat. No. 4,465,487 assigned to Terumo discloses fabricating steam autoclavable medical containers by irradiating ethylene vinyl acetate copolymers with high energy (2 Mev) electron beams at doses between 50 kGy and 100 kGy to achieve gel contents of between 50% and 85%. The '487 Patent discloses that if the EVA sidewalls of the container are irradiated to achieve a gel content of about 50% or higher before being sealed together they are easily peeled apart. (Col. 4, lines 20-30). Accordingly, the '487 Patent discloses irradiating the sidewalls of the container after sealing the container into a pouch leaving only a port area unsealed.

[0012] Similarly, U.S. Pat. No. 4,453,940 discloses fabricating medical containers from EVA and other materials. The '940 Patent also discloses the step of increasing the autoclave resistance of EVA by cross-linking the material with high energy electron beam. The '940 Patent warns that if the cross-linking exceeds 50% the use of heat sealing becomes impossible. (Col. 4, lines 27-35).

[0013] U.S. Pat. No. 4,401,536 discloses crosslinking semi-rigid containers composed of films of polypropylene and EVA or EEA. This patent does not disclose the use of ethylene alpha olefins with polypropylene. It also discloses that irradiation before forming results in articles with poor heat sealability (Col.4, lines 25-28).

[0014] U.S. Pat. Nos. 4,892,604 and 5,066,290 both assigned to the present assignee, disclose a medical container with a coextruded high density polyethylene skin layer and a core layer of an ethylene vinyl acetate copolymer having about 18% vinyl acetate content. After the container is fabricated by conventional radio frequency heat seal, the assembly is subjected to ionizing radiation of about 100 kGy from a high energy electron beam accelerator of about 5 Mev. The high density polyethylene layer acts as a moisture and gas transmission barrier to maintain the sterile fluid content at a relatively constant concentration as required by various pharmacopoeia of the world. However, several serious deficiencies were apparent in this material construction: 1) to fabricate a container from this material construction the container must be fabricated before the cross-linking process, since the cross-linked EVA layer is difficult if not impossible to seal (this renders the manufacturing process very inefficient); and 2) the radiation dose required for sufficient cross-linking also releases significant quantities of acetic acid—a by-product of the radiation exposure. Since the HDPE presents a barrier to gas transmission, the trapped acetic acid can render the fluid contents quite acidic—a very undesirable outcome.

[0015] U.S. Pat. No. 4,643,926 assigned to W. R. Grace discloses fabricating a medical solution container from a multilayered material where, in certain embodiments, the layer intended to be heat sealed is constructed with polypropylene as the main ingredient. Since it is well known that polypropylenes undergo chain scission when exposed to radiation, the heat seal layer remained thermoplastic and capable of being heat-sealed to similar surfaces. Therefore, the entire multilayer film can be heat-sealed and survive autoclaving. However, the complexity of the multilayer construction and the possible need of washing and incorporating acid scavenging compounds in the film (See U.S. Pat. No. 5,445,893) to remove the acidic by-products of irradiating EVA renders the process quite complicated and the cost very high. Further, since the film is constructed of several very dissimilar materials, process recycling of the edge trim and other film scraps is very difficult and impractical without greatly reducing the optical and mechanical properties.

[0016] U.S. Pat. No. 5,055,328 discloses a multilayer differentially cross-linked film where the heat-sealed layer contains additional antioxidants to retard cross-linking and to facilitate heat-sealing post cross-linking. Likewise, Canadian Patent 1,125,229 discloses another differential cross-linked multilayer film where the outer layer contains a cross-link enhancer. However, these constructions are all multilayer constructions and do not address the issue of self adhesion during autoclaving.

[0017] U.S. Pat. No. 4,724,176 to Sun discloses a multilayer, oriented, heat shrinkable container with a radiation cross-linked outer layer and, by controlling the irradiation process, a non cross-linked inner seal layer. The inner and outer layers can be of EVA copolymers. This container is designed to shrink upon application of heat, and, therefore,

would be unsuitable for a container that must maintain substantially its entire volume after an autoclave process.

[0018] U.S. Pat. No. 4,550,141 discloses polymer blends of ionomers with propylene and α -olefin copolymers. The '141 Patent also discloses single-layered and multiple-layered films made from the blends. The '141 patent discloses forming peel seals using these films wherein it is desirable to have a consistent peel strength over a wide heat sealing temperature range (e.g., a range of at least 10° C.). The '141 Patent does not disclose exposing the blends or films to radiation to cause cross-linking. Further, the '141 Patent states that it is not an object to provide a peelable seal that is capable of withstanding steam sterilization (col. 1, lines 55-57).

[0019] The present invention provides polymeric materials that are, overall, superior to those materials, of which we are aware, which have been heretofore known in the art or have been commercially used or marketed. The properties of such materials include flexibility, optical transparency for visual inspection, and sufficient thermal resistance to withstand a steam sterilization process at temperatures up to 121° C. without experiencing significant distortion or self adhesion. The materials should also be non-oriented, non-adherent and capable of being sealed using heat sealing techniques. The materials should also be substantially free of low molecular weight leachable additives, and capable of safe disposal by incineration without the generation of significant amounts of corrosive inorganic acids. Finally, the material should serve as a cost-effective alternative to various PVC formulations currently being used for medical devices.

[0020] U.S. Pat. No. 5,879,768 discloses a pouch for packaging flowable materials fabricated from a material having a seal layer of a polymeric composition comprising: (A) 10 to 100 percent of a mixture of (1) from 5 to 95% of at least one homogeneously branched substantially linear ethylene/ α -olefin interpolymers, and (2) from 5 to 95% of high pressure low density polyethylene having a density from 0.916-0.930 g/cc; and (B) from 0-90% of one polymer selected from the group consisting of an ultra low density polyethylene, a linear low density polyethylene, a high pressure low density polyethylene, an ethylene vinyl acetate copolymer, and a homogeneously branched linear ethylene polymer. The '768 Patent does not disclose exposing this film to radiation nor does it disclose blending the homogeneously branched, substantially linear ethylene/ α -olefin interpolymers with polypropylene.

[0021] When more than one polymer is blended to form an alloying composition, it is difficult to achieve all of the above objectives simultaneously. For example, many alloys produce significant light scattering; thus, they fail to meet the optical clarity objective. The light scattering intensity (measured by haze) depends on the domain size of components in the micrometer (μ) range, and the proximity of the refractive indices of the components. As a general rule, the selection of components that can be satisfactorily processed into very small domain sizes, and yet with a minimum of refractive index mismatches, is a difficult task.

[0022] There are innumerable uses for such polymer films. One conventional use is to fabricate a peelable seal. A peelable seal is the seal or joint between two films produced by heat-sealing, or by any sealing method known in the art,

the seal or joint thus formed having the property of being able to open in the original plane of the joining of the two films by a pulling force without destroying the integrity of the films or the peripheral/permanent seal. Prior to the present invention, peelable seals were formed by sealing multilayer films, as disclosed in U.S. Pat. Nos. 5,904,425; 5,893,645; and 5,887,980, which are incorporated herein by reference and made a part hereof. One problem, though, with current peelable seals is that the peel strength is unpredictable because of low manufacturing tolerances for processing window variances. For example, the peel strength could be excessively weak, which might not provide a hermetic seal, or excessively strong, which might be difficult to break.

[0023] U.S. Pat. Nos. 4,808,662 and 4,189,519 disclose a peelable seal characterized by a nearly constant peel strength over an extended sealing temperature range. A variety of other references disclose sealable films capable of forming peelable seals, such as U.S. Pat. Nos. 4,916,190; 4,784,885; 4,539,263; 4,414,053 and 3,879,492. However, none of the foregoing references teach forming a peelable seal from a monolayer film where the components of the film have distinct melting point temperatures, where the peelable seal has a nearly constant peel strength before and after autoclaving, and where the monolayer film forming the peelable seal can subsequently be formed into a container. The present invention is provided to solve these and other problems.

SUMMARY OF THE INVENTION

[0024] The present invention provides polymer blends having a first component of a polymeric material capable of being cross-linked and selected from the group consisting of an ethylene containing polymer, the first component present in an amount by weight of the blend from about 50% to about 95%, the first component having a first melting point temperature determined by DSC; and a second component of a non-readily cross-linkable polymeric material and selected from the group consisting of propylene containing polymers and methyl pentene containing polymers, the second component being present in an amount by weight of the blend from about 50% to about 5%, the second component having a second melting point temperature determined by DSC; and a portion of the first component being cross-linked and the second component is essentially free of cross-linking.

BRIEF DESCRIPTION OF THE DRAWINGS:

[0025] FIG. 1 is a cross-sectional view of a monolayer film of the present invention;

[0026] FIG. 2 is a cross-sectional view of a multiple layered film of the present invention;

[0027] FIG. 3 is a material container fabricated from a film of the present invention;

[0028] FIG. 4 is an I.V. fluid administration set;

[0029] FIG. 5 is a peritoneal dialysis container and tubing set;

[0030] FIG. 6 is a dual chamber bag with a peelable seal separating the chambers;

[0031] FIG. 7 shows a general DSC plot depicting a peel seal heat sealing window defined between two melting point temperatures;

[0032] FIG. 8 shows a cross-sectional view of a tubing of the present invention;

[0033] FIG. 9 shows a plot of peel seal force versus sealing temperature for a film before and after autoclaving process; and

[0034] FIG. 10 shows a graph showing average peel force versus sealing temperature for films having various degrees of surface roughness.

DETAILED DESCRIPTION OF THE INVENTION

[0035] The present invention is susceptible of embodiments in many different forms. Preferred embodiments of the invention are disclosed with the understanding that the present disclosure is to be considered as an exemplification of the principles of the invention and is not intended to limit the broad aspects of the invention to the embodiments illustrated.

[0036] I. Polymer Blends and Monolayer Films Therefrom

[0037] a. First Polymer Blend

[0038] FIG. 1 shows a monolayer film 10 of the present invention. The monolayer film 10 is fabricated from a polymer blend having a first component and a second component. The first component is selected from the group of: (1) ethylene and α -olefin interpolymers having a density of less than about 0.915 g/cc, (2) ethylene and lower alkyl acrylate interpolymers, (3) ethylene and lower alkyl substituted alkyl acrylate interpolymers and (4) ionic polymers, commonly referred to as ionomers. The first component is present in an amount from about 99% to about 55% by weight of the film, more preferably from about 60%-85% and most preferably from about 65%-80%.

[0039] The second component is selected from the group consisting of: (1) propylene containing polymers, (2) butene containing polymers, (3) polymethyl pentene containing polymers, (4) cyclic olefin containing polymers and (5) bridged polycyclic hydrocarbon containing polymers. The second component is present in an amount by weight of the film from about 45% to about 1%, more preferably from about 15%-40% and most preferably from about 20%-35%.

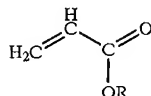
[0040] The film has a modulus of elasticity when measured in accordance with ASTM D882 of less than about 60,000 psi, an internal haze when measured in accordance with ASTM D 1003 of less than about 25%, self adhesion ranking greater than about two (as defined below), slight or no adhesion to overpouch materials, has a sample creep at 120° C. at about 27 psi loading of less than or equal to 150%, and the film can be heat sealed into a container having seals wherein the seals remain intact when a liquid filled container is autoclaved at temperatures from about 100° C. to about 121° C. for one hour.

[0041] As used herein, the term "interpolymer" includes copolymers, terpolymers either random or block.

[0042] Suitable ethylene and α -olefin interpolymers preferably have a density, as measured by ASTM D-792 of less than about 0.915 g/cc and are commonly referred to as very low density polyethylene (VLDPE), ultra low density ethylene (ULDPE) and the like. The α -olefin should have from 3-17 carbons, more preferably from 4-12 and most prefer-

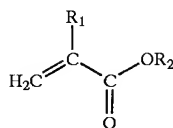
ably 4-8 carbons. In a preferred form of the invention, the ethylene and α -olefin copolymers are obtained using single site catalysts. Suitable single site catalyst systems, among others, are those disclosed in U.S. Pat. Nos. 5,783,638 and 5,272,236. Suitable ethylene and α -olefin copolymers include those sold by Dow Chemical Company under the AFFINITY tradename, Dupont-Dow under the ENGAGE tradename and Exxon under the EXACT and PLASTOMER tradenames.

[0043] The term "lower alkyl acrylates" refers to comonomers having the formula set forth in Diagram 1:



[0044] The R group refers to alkanes having from 1 to 17 carbons. Thus, the term "lower alkyl acrylates" includes but is not limited to methyl acrylate, ethyl acrylate, butyl acrylate and the like.

[0045] The term "alkyl substituted alkyl acrylates" refers to comonomers having the formula set forth in Diagram 2:



[0046] R_1 and R_2 are alkanes having 1-17 carbons and can have the same number of carbons or have a different number of carbons. Thus, the term "alkyl substituted alkyl acrylates" includes but is not limited to methyl methacrylate, ethyl methacrylate, methyl ethacrylate, ethyl ethacrylate, butyl methacrylate, butyl ethacrylate and the like.

[0047] Suitable propylene containing polymers include those selected from the group consisting of homopolymers of polypropylene, copolymers and terpolymers of propylene with one or more comonomers selected from α -olefins having from 2-17 carbons. Suitable polypropylene copolymers and terpolymers include random or block propylene and ethylene copolymers or random or block propylene/ethylene/butene terpolymers. Suitable propylene and α -olefin copolymers are sold by Basell under the tradename PRO FAX, PRO FAX ULTRA and CATALLOY.

[0048] The present invention also contemplates using blends of propylene containing polymers as the second component of the film. In a preferred form of the invention the blends include at least a first propylene containing polymer and a second propylene containing polymer. The first propylene containing polymer and the second propylene containing polymer can be selected from the propylene homopolymer, copolymers and terpolymers set forth above. In a preferred form of the invention the first propylene containing polymer differs from the second propylene containing polymer in at least one of two ways. The first difference is the first propylene containing polymer preferably should have a melt flow rate of from about 3 times

greater and more preferably from about 5 times greater than the melt flow rate of the second propylene containing polymer. The second difference is the first propylene-containing polymer preferably has a melting point from at least about 5° C. higher and more preferably from at least about 10° C. higher than that of the second propylene containing polymer. The melting point is measured in accordance with ASTM D3417 (Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry). The first propylene containing polymer can differ from the second propylene containing polymer by the first difference, by the second difference or by both.

[0049] Suitable homopolymer and copolymers of cyclic olefins and bridged polycyclic hydrocarbons and films thereof can be found in U.S. Pat. Nos. 5,218,049, 5,854,349, 5,863,986, 5,795,945, 5,792,824; and European Patent numbers EP0 291,208, EP0 283,164, EP 0 497,567 which are incorporated in their entirety herein by reference and made a part hereof.

[0050] In a preferred form of the invention, suitable cyclic olefin monomers are monocyclic compounds having from 5 to about 10 carbons in the ring. The cyclic olefins can be selected from the group consisting of substituted and unsubstituted cyclopentene, cyclopentadiene, cyclohexene, cyclohexadiene, cycloheptene, cycloheptadiene, cyclooctene, cyclooctadiene. Suitable substituents include lower alkyl, acrylate derivatives and the like.

[0051] In a preferred form of the invention, suitable bridged polycyclic hydrocarbon monomers have two or more rings and more preferably contain at least 7 carbons. The rings can be substituted or unsubstituted. Suitable substituents include lower alkyl, aryl, aralkyl, vinyl, allyloxy, (meth)acryloxy and the like. The bridged polycyclic hydrocarbons are selected from the group consisting of those disclosed in the above incorporated patents and patent applications. Suitable bridged polycyclic hydrocarbon containing polymers are sold by Ticona under the tradename TOPAS, by Nippon Zeon under the tradename ZEONEX and ZEONOR, by Daikyo Gomu Seiko under the tradename CZ resin, and by Mitsui Petrochemical Company under the tradename APEL.

[0052] In a preferred form of the present invention a monolayered film formed from one of the above blends will have the following physical characteristics: (1) a modulus of elasticity when measured in accordance with ASTM D882 of less than about 60,000 psi, (2) an internal haze when measured in accordance with ASTM D1003 of less than about 25%, (3) self adhesion ranking greater than about two as defined below, (4) essentially no adhesion to overpouch materials, (5) has a sample creep at 120° C. at about 27 psi loading of less than or equal to 150%, and (6) the film can be heat sealed into a container having seals wherein the seals remain intact when a liquid-filled container is autoclaved at 121° C. for one hour.

[0053] The film is also sufficiently flexible to construct flowable material containers. The film has a modulus of elasticity of less than about 60,000 psi, more preferably less than about 40,000 psi, even more preferably less than about 30,000 and most preferably less than about 20,000 psi when measured in accordance with ASTM D-882. When the flowable material container is an I.V. container it is desirable the container collapse or substantially collapse upon drain-

ing, and, therefore, should have a modulus of elasticity of less than about 40,000 psi, more preferably less than about 30,000 psi, and even more preferably less than about 20,000 when measured in accordance with ASTM D-882.

[0054] For the purposes of this invention, self-adhesion is defined as the tendency of the film to adhere to itself during autoclaving. This property can be determined with the following test. Film strips are cut 8"x2", with the larger dimension in the machine direction. These strips are rolled into 2" long tubes approximately 0.5" in diameter. The wound film is held in place by compressing the film layers together at one end with a paper clip. The tubes are then placed in a steam autoclave at 121° C. for 30 minutes. The samples are allowed to cool for at least one hour. The film is then unwound. The resistance to unwinding and relative damage to the film is ranked as shown in Table 1 as follows:

[0055] Table 1

[0056] Rank Observed Result

[0057] (1) The film cannot be unwound without destroying the film.

[0058] (2) The film is difficult to peel and significant surface damage results.

[0059] (3) Some resistance to peeling and minor surface damage are noted.

[0060] (4) Slight resistance to peeling noted with little or no surface damage.

[0061] (5) No peel resistance and no surface damage noted.

[0062] Ranks are determined by three or more individuals and recorded as an average.

[0063] Adhesion to over pouch materials is determined by the following qualitative test. One inch wide strips of film are sealed into typical over pouch bags (medium or high density polyethylene). The over pouch bag is then placed into a laboratory autoclave at 252° F. and 24.5 psig gauge pressure for one hour. After autoclaving, the bags are cut open and the strips removed. If the films separate from the over pouch without leaving damage marks on the film surface, a ranking of no adhesion (N) is given. If the film separation produces visible damage, a ranking is given (Y) indicating that tack to the over pouch is present. A ranking to indicate slight adhesion (S) can also be given.

[0064] Creep properties were determined at 120° C. by clamping film strips having a thickness from about 5 mils to about 15 mils in a temperature controlled oven and loading with weights to produce a stress of about 27 psi. After loading for 40 minutes, the film strips were removed and the dimensional changes in a pre-marked one inch gap were recorded.

[0065] The film is capable of being sealed using standard heat sealing techniques. An adequate heat seal is formed when a fluid container, such as the one shown in FIG. 3, is fabricated from the film by sealing peripheral edges to define a centrally disposed fluid chamber. The container is filled with water and subjected to a standard autoclave sterilization process. Adequate heat seals remain intact upon completion of the autoclave cycle.

[0066] The films of the present invention have a haze of less than about 25% and most preferably less than about 15% when measured in accordance with ASTM D1003. For the purposes of this invention, internal haze is defined as the haze value measured when both film surfaces have been wetted with isopropyl alcohol.

[0067] b. Second Polymer Blends and Cross-linking

[0068] The present invention also provides other polymer blends suitable for fabricating a monolayer film, a multilayer film, a peel-seal film, a food or medical product container, a multichamber container, a multichamber peel seal container, an I.V. bag, a dialysis container, a nutritional-fluids container, and the like. The polymer blends have at least two components. The first component is a readily cross-linkable polymer and more preferably an ethylene-containing polymer. The second component is a non-readily cross-linkable polymer and more preferably a propylene-containing polymer. The blend is exposed to radiation to cross-link the first component but not the second component. The first component has a first melting point temperature determined by differential scanning calorimetry (DSC) and the second component has a second melting point temperature determined by DSC that is higher than the first melting point temperature. (See FIG. 7)

[0069] What is meant by the term cross-link is chemical linkages formed between different polymer molecules or between different segments of the same polymer molecule. Cross-linked polymers will show a significant increase in melt viscosity from a non-cross-linked version of the same polymer. What is meant by the term "readily cross-linkable polymer" is a polymer that can be cross-linked using standard cross-linking techniques. What is meant by "standard cross-linking techniques" are those polymer processing techniques that are well known in the art. Standard cross-linking techniques includes: (1) radiation exposure type cross-linking techniques, and (2) chemical-exposure type cross-linking techniques. Radiation-exposure type cross-linking techniques includes exposing a polymer to: gamma radiation, electron beam radiation, ultra-violet radiation or electromagnetic energy in other frequency ranges that are effective to cause cross-linking. Chemical-exposure cross-linking techniques include using peroxides, silanes, multifunctional acrylates, sulfur or other chemical cross-linking agents effective to cause cross-linking.

[0070] What is meant by the term "non-readily cross-linkable polymer" is a polymer that does not increase substantially in weight average molecular weight when exposed to the cross-linking techniques set forth above.

[0071] The first component is present in an amount by weight of the polymer blend from a minimum point starting from about 50% and successively incrementally increasing by 5% the minimum point (i.e., 55%, 60%, 65%, etc.) to a maximum of 95%. Thus, for example, the first range is from about 50% to about 95%. The second range is from about 55% to about 95% and the final range is from about 90% to about 95%. In yet another preferred form of the invention the first component will be present in an amount by weight of from about 55% to about 90%, more preferably from about 60% to about 80%, and even more preferably from about 65% to about 75%.

[0072] The first component can be a single ethylene-containing polymer or a blend of two or more ethylene

containing polymers which in sum constitute by weight the ranges set forth for the first component. The melting point temperature of such a blend will show a single distinct composite melting point or a peak for each ethylene-containing polymer of the blend or a combination of the same.

[0073] Suitable ethylene-containing polymers include those selected from the group consisting of ethylene homopolymers and ethylene copolymers set forth above. Suitable ethylene and α -olefin copolymers will have a density of less than about 0.915 g/cc, more preferably less than about 0.905 g/cc, and most preferably less than about 0.900 g/cc. Suitable polymers include, but are not limited to, ultra low-density polyethylene (ULDPE), ethylene-propylene rubber (EPR), and ethylene propylene diene terpolymer (EPDM). Preferably, the ethylene-containing polymers are those sold by Dow Chemical Company under the AFFINITY tradename, most preferably Affinity PL 1880 and VP 8770, and by Dupont-Dow under the ENGAGE tradename, most preferably Engage 8003.

[0074] The second component will constitute the remaining weight-percent portion of the blends and will be present singularly or in sum the converse weight percentage ranges from those set forth above for the first component. Accordingly, if the first component is present from about 50% to about 95% the second component or the sum of the additional components will be the converse or from about 5% to about 50%.

[0075] The second component may be a single propylene-containing polymer or a single methyl-pentene-containing polymer. The second component can also be a blend of two or more propylene-containing polymers, two or more methyl-pentene-containing polymers or a blend of at least one propylene-containing polymer and at least one methyl-pentene-containing polymer.

[0076] Suitable propylene-containing polymers include those selected from the group consisting of homopolymers of polypropylene, copolymers and terpolymers of propylene with one or more comonomers selected from α -olefins having from 2-18 carbons. Suitable polypropylene copolymers and terpolymers include random or block propylene and ethylene copolymers or random or block propylene/ethylene/butene terpolymers. Suitable propylene and α -olefin copolymers are sold by Basell under the tradename PRO FAX, preferably PRO FAX SA-861 and by Exxon as Exxon PP3505GE1. In a preferred form of the invention, the second component will have a distinct melting point temperature, a distinct composite melting point temperature or a melting point temperature associated with each of the sub-components of the second component, or a combination of the same, determined by DSC of equal to or higher than about 135° C. Further, in a preferred form of the invention the first component will have a modulus of elasticity of less than about 200,000 psi, more preferably less than about 150,000 psi, and most preferably less than about 100,000 psi.

[0077] Suitable methylpentene-containing polymers include homopolymers of 4-methylpentene-1; copolymers and terpolymers of methylpentene with one or more comonomers selected from α -olefins having from 2-18 carbons. A preferred methylpentene-containing polymer is sold by Mitsui Petrochemical, Ltd. under the tradename TPX™.

[0078] In a preferred form of the invention the first component will constitute what is known as the continuous

phase and the second component or other additional components will constitute a dispersed phase or dispersed phases as the case may be.

[0079] The second component of the polymer blend is selected from the group consisting of propylene-containing polymers and methylpentene-containing polymers. The second component is present in the amounts set forth above.

[0080] It is also contemplated additional polymer processing components can be added to the blends of the present invention. For example it may be desirable to add a fatty acid amide or diatomaceous earth. Suitable fatty amides include those derived from fatty acids having from 10 to 30 carbons and most preferably is derived from erucic acid.

[0081] The second polymer blend can be fabricated into a monolayer film using standard polymer processing techniques such as extrusion.

[0082] Referring now to FIG. 7 showing a plot from a differential scanning calorimeter of a two-component polymer blend of the present invention fabricated into a monolayer film. The first melting point temperature and the second melting point temperature are referred to respectively as 100 and 102. The temperature range from and including the first melting point temperature 100 to a point just lower than the second melting point temperature 102 defines a peel seal heat sealing window 104 wherein die sealing temperatures will provide a peel seal and at temperatures above the second melting point temperature and below the temperature where the polymer burns will provide a permanent seal.

[0083] This material property allows for formation of both peel seals and permanent seals using the same film. For example, a monolayer film of the present invention can be folded upon itself to define a layered structure having both a peel seal in a first location and a permanent seal in a second location spaced a distance from the first location.

[0084] II. Polymer and Film Processing

[0085] To produce the films of the present invention from the above-described polymer blends, raw materials are fed into an extrusion hopper at the desired mix ratio employing weight feeders. The materials are extruded using an extrusion die to produce a mono-layer film. The film is irradiated with a suitable energy source and then sealed to form a fluid container. The raw materials can also be pre-compounded before extrusion employing a single screw, twin screw or other compounding methods familiar to those skilled in the art. Other polymer processing techniques may also be used to fabricate the film, either sheet film or tube film, of the present invention including blow molding, blown extrusion, thermoforming, calendaring, compression molding or other polymer processing techniques well known in the art.

[0086] The film can be cross-linked using standard cross-linking techniques including: (1) radiation exposure type cross-linking techniques, (2) chemical-exposure type cross-linking techniques or (3) a combination of both techniques. Radiation-exposure type cross-linking techniques includes exposing a polymer to: gamma radiation, electron beam radiation, ultra-violet radiation or electromagnetic energy in other frequency ranges that are effective to cause cross-linking. Chemical-exposure cross-linking techniques

include using peroxides, silares, multifunctional acrylates, sulfur, or other chemical cross-linking agents.

[0087] The preferred method of irradiating the film is to expose it to an electron beam with beam energy from about 150 Kev-10 Mev, more preferably from 200-300 Kev and a dosage from about 20 kGys to about 200 kGys and more preferably from about 60-150 kGys. To reduce or minimize the oxidative degradation of the film during and subsequent to electron beam exposure, it is desirable to reduce the partial pressure of oxygen in the area surrounding the film being exposed to the radiation. The oxygen partial pressure may be reduced by applying a vacuum or by applying another gas such as nitrogen under pressure or other known techniques for accomplishing this goal. In a preferred form of the invention the oxygen concentration during a nitrogen flush is less than about 400 ppm, more preferably less than about 100 ppm and more preferably less than about 40 ppm.

[0088] III. Multilayer Films

[0089] FIG. 2 shows an example of a multilayer film 20 including layer 12 of the mono-layer described above. In a preferred form of the invention the monolayer shall be the seal layer. The multilayer film 20 can include any additional layer 14 or combination of additional layers selected from layers such as a skin layer, a radio frequency susceptible layer, a water vapor barrier layer, a gaseous barrier layer, a scrap layer, a seal layer and a core layer to name a few.

[0090] The skin layer can be added to increase the scuff resistance of the film. The skin layer can be an olefin material such as homopolymers and copolymers of propylene and ethylene. The skin layer may also be a polyester, copolyester, polyamide or copolyamide. The term "copolyester" and the like is applied to polyesters synthesized from more than one diol and a dibasic acid. Copolyesters as used herein may also be characterized as copolymers of polyether and polyethylene terephthalate. More preferably copolyesters as used herein may be characterized as polymeric materials derived from 1,4 cyclohexane dimethanol, 1,4 cyclohexane dicarboxylic acid, and polytetramethylene glycol ether, or equivalents of any of the above, as reactants. Suitable copolyesters therefore include polyester ethers such as PCCE.

[0091] Suitable water vapor barriers include but are not limited to HDPE, MDPE and polyester (PET, PBT, PEN, etc.)

[0092] Suitable gaseous barriers are those that inhibit the passage of oxygen, carbon dioxide or other gasses. Suitable gas barriers include but are not limited to polyesters, EVOH, and polyamides.

[0093] Scrap material generated prior to irradiation can be incorporated into one or more layers.

[0094] IV. Flowable Material Containers FIG. 3 shows a flowable materials container and particularly an I.V. container 30 made from a monolayer film or a multilayered film described above. FIG. 4 shows an I.V. administration set 40 and FIG. 5 shows a peritoneal dialysis set 50 fabricated from the polymer blends of the present invention. The present invention further contemplates fabricating medical tubing (FIG. 8) from the blends of the present invention. It is contemplated that the radiation treatment of tubing will differ from films due to the increased thickness and round

shape of tubing but tubing can be effectively treated within the radiation energy ranges set forth above for the film.

[0095] What is meant by "flowable material" is a material that will flow by the force of gravity. Flowable materials therefore include both liquid items and powdered, lyophilized or granular items and the like.

[0096] The container 30 has sidewalls 32 placed in registration and sealed along peripheral edges to form a permanent peripheral seal 33 to define a chamber 34 for containing flowable materials such as fluids or granular material. For containers made through blow molding only or blown extrusion process longitudinal edges would be sealed to complete the container. A port tube 36 or multiple port tubes are provided to fill and empty the contents of the container 30. The sidewalls and port tube can be fabricated from one of the monolayer or multiple layered films set forth above. Surprisingly, the medical articles fabricated from the blends and films described above can be heat sealed even though the film has been irradiated with electron beam radiation.

[0097] In a preferred form of the invention, the film and containers will be capable of withstanding a steam sterilization process of up to at least 130° C. and more preferably from about 100° C. to about 126° C. and even more preferably from about 100° C. to about 121° C. Heat seals can be achieved using standard heat sealing techniques known to those skilled in the art.

[0098] V. Multi-Chamber Containers Incorporating Peel Seal

[0099] FIG. 6 shows a dual chamber container 70 having a first chamber 72 and a second chamber 74 separated by a peelable seal 76. The container sidewalls 75 are fabricated from one of the polymer blends, monolayer films or multiple layered films set forth above. Dual chamber containers can be used for numerous applications such as separately housing two components for mixing later. Typically, one of the chambers will contain a liquid. By pressing on the container sidewall 75 over the liquid containing chamber the liquid contents will flow toward the peelable seal 76 and by applying sufficient pressure the seal 76 will rupture to allow mixing of the components stored in the separate chambers.

[0100] While FIG. 6 shows only one peelable seal 76, it is contemplated that numerous peelable seals could be provided to create numerous chambers. Further, FIG. 6 shows the peelable seal running between lateral edges. It is also contemplated that the peelable seals could extend between longitudinal edges or simply around an area not intersecting the permanent peripheral seam 33 to define a chamber.

[0101] The peelable seal 76 may be created simultaneously with sealing the peripheral sidewalls or before or after the creation of the permanent peripheral seals. The peelable seal 76 can be created by controlling sealing conditions. Peelable seals can be created with the application of lower temperature and pressure than employed to provide the permanent peripheral seal 33 or by shortening the sealing times from that used to provide the permanent seal or the like. Further enhancement of the peel characteristics can be obtained with localized modification of the film surface characteristics (corona or other suitable treatment). It is contemplated that the container can be sealed using

ultrasonic welding techniques, conduction heat sealing techniques and other sealing techniques well-known in the art.

[0102] The present invention contemplates that a peelable seal can be formed between films of the present invention. It is also contemplated that the films of the present invention can be peel sealed to other polymeric films, paper products or metal foils. It is further contemplated the films and sealing techniques disclosed herein can be used to form peel seals between materials which would otherwise not be capable of forming a peel seal. This can be accomplished by attaching the films of the present invention to the material not suitable for forming a peel seal along a line where the peel seal is to be formed and then sealing along the line where the peel seal material is present.

[0103] According to a preferred form of the invention, the peel seal 76 is formed by sealing the peel seal 76 at a temperature in the peel seal heat sealing window 104 positioned between the first and second melting point temperatures 100 and 102 respectively. For instances where the first component is a blend of more than one ethylene-containing polymer having more than one distinct melting point peak the peel seal heat sealing window 104 will extend between the higher melting point temperature peak of the first component to the lowest melting point peak of the second component. In a preferred form of the invention, the peel seal heat sealing window 104 will include a temperature used to steam sterilize the films or containers made therefrom. The peel seal heat-sealing window should include temperatures from about 75° C. to about 135° C., more preferably from about 100° C. to about 130° C. and even more preferably from about 110° C. to about 125° C. It has been found that in sealing at various temperatures within the peel seal heat sealing window provide a nearly constant or essentially constant peel strength. Further, it has been found that it is possible to achieve a nearly constant peel strength when comparing a peel seal formed by sealing in the heat sealing window before and after the autoclaving or steam sterilization process (FIG. 9). What is meant by nearly constant or essentially constant is that the strength of the peelable seal increases or decreases by less than about 30%, more preferably less than about 20% and most preferably less than about 10% before and after autoclaving when sealed at a temperature in the peel seal heat sealing window 104.

[0104] In a preferred form of the invention the peel seals of the present invention will be capable of adhesive release as opposed to cohesive release. The term adhesive release means the peel seal can be activated (peeled apart) and the line along which the peel seal existed has no visible fibrils or other visible particulate matter remaining from the material that formed the seal. The term cohesive release is meant to refer to a peel seal that upon activation has visible fibrils or other particulate matter in the general area where the peel seal extended prior to activation.

[0105] Additionally, the present invention contemplates that the films could be subjected to a sealing process at a temperature above the second melting point temperature to form a permanent seal. In instances where there is more than one propylene-containing polymers having two or more distinct melting points then a permanent seal can be formed by a sealing process above the lower of the propylene melting point temperatures.

[0106] VI. Surface Texture

[0107] The present invention further provides for optionally providing the films with a surface texture or roughness. The amount of surface roughness can be quantified by surface haze values measured by ASTM 1003 and by profilometer roughness Ra values. These films were also tested for peel seal strength before and after autoclaving.

[0108] The internal haze is determined after wetting with isopropyl alcohol. The surface haze is total haze-internal haze. Profilometer readings are measured by a Sheffield Profilometer (Warner & Swasey) with a type G tracer. Ra is roughness average value—the arithmetic average height if roughness irregularities measured from a mean line within the evaluate length (L)

$$\text{where } Ra = 1/L \int_0^L |y| dx$$

[0109] FIG. 10 shows a plot of three films having varying amounts of surface texture but otherwise of the same material. The first plot 150 has a low surface roughness, plot 152 has a medium surface roughness and plot 154 has a high surface roughness. Peel seal strengths of these films were measured by taking two films of the same material, positioning them in registration and forming a weld within the temperatures of the peel seal window. The films were peeled using an Instron device and the strength required to peel the seal was reported.

[0110] To form a peel seal it is desirable to have an average peel seal strength of less than about 50 N/15 mm, more preferably less than about 40 N/15 mm and even more preferably less than about 30 N/15 mm. The peel seal should also have a peel strength in excess of about 3 N/15 mm.

[0111] Surface roughness can be imparted on the film using textured rollers or other such technique well known in the art.

VII. EXAMPLES

First Set of Examples

[0112] The films identified in the tables below were fabricated into a monolayer film using an extrusion process. The film was exposed to electron beam radiation having an acceleration voltage of from 200 Kev to 300 Kev for a dose set forth in the tables that follows:

TABLE 2

FORMULA	1	2	3	4	5	6	7	8	9	10
DuPont/Dow Engage 8003	100	95	90	80						70
Dow Affinity PL-1880					100	95	90	80	70	
Exxon PP3505GE1		5	10	20						

TABLE 2-continued

FORMULA	1	2	3	4	5	6	7	8	9	10
Basell SA-861						5	10	20	30	20
Basell SG-982										10
Self adhesion rank - 100 kGy	1	2	3.7	4	1	NA	1	2	4	NA
150 kGy	1	2	4.5	5	1	NA	1.3	2.3	3.3	NA
200 kGy	1	3.3	4.7	5	1	1.7	2	2	4	NA
Tack to over pouch - 100 kGy	Y	S	N	N	Y	NA	Y	S	N	NA
150 kGy	Y	S	N	N	Y	NA	Y	N	N	NA
200 kGy	Y	S	N	N	Y	NA	Y	N	N	NA
120° C. Creep (%) 0 kGy	NA	NA	NA	NA	NA	NA	Melts	NA	550	NA
100 kGy	200	138	88	41	263	NA	216	98	28	NA
150 kGy	63	38	31	18	43	NA	31	25	13	NA
200 kGy	25	13	16	16	21	22	16	9	22	NA
Autoclavability 100 kGy	NA	NA	Y	Y	NA	NA	NA	Y	Y	Y
150 kGy	NA	NA	Y	Y	NA	NA	NA	Y	Y	Y
Internal Haze (ASTM D1003)	1	1.2	1.6	2.8	2.7	2.7	3.5	4.3	4.8	2.2
Tensile modulus (psi) (ASTM D882)	2860	3800	6650	16260	6110	NA	12830	19810	28820	21060

Dow Affinity PL 1880 is a ULDPE having a density of 0.902 g/cc.
 DuPont Dow Engage 8003 is a ULDPE having a density of 0.885 g/cc.
 Exxon PP305GE1 is a homopolymer of propylene (MFR 440).
 Montell SA-861 is a propylene and ethylene copolymer (MFR 6.5).
 Montell SA 982 is a propylene and ethylene copolymer (MER 100).
 "NA" means not available.

Second Set of Examples

[0113] Table 3 contains data on a peelable seal formed from two monolayer films of the same material. The monolayer films were exposed to electron beam radiation having an acceleration voltage of from 250 Kev for a dose of 120 KGys.

TABLE 3

Formula	11	12
DuPont-Dow Engage 8003 or Dow Affinity VP 8770	40	40
Dow Affinity PL1880	25	25
1 ST TM (° C.) by DSC	94	94
Exxon PP 3505GE1	5	—
Basell SA-861	30	35
2 nd TM (° C.) by DSC	153	148
Peel Seal Strength (Newton/15 mm) Before Autoclaving [#]	15-17	18-20
Peel Seal Strength (Newton/15 mm) After Autoclaving [#]	15-16	18-19

[#]: Peel seal was conducted at about 121 C.

Third Set of Examples

[0114] FIG. 10 shows a plot of three films having varying amounts of surface haze and profilometer measurements. Films having the formulations reported in Table 4 were placed in registration with one another and a heat seal was formed at 121° C. The amount of force to separate the seal was measured on an Instron and is tabulated in Table 4 below. These examples demonstrate the effect surface texture has on peel seal strength. It can be seen from the data, as the surface roughness increases the peel seal force decreases.

TABLE 4

Formula	13	12	14
DuPont-Dow Engage 8003 or Dow Affinity VP 8770	40	40	40
Dow Affinity PL1880	25	25	25
1 ST TM (° C.) by DSC	94	94	94
Basell SA-861	35	35	35
2 nd TM (° C.) by DSC	148	148	148
Profilometer Roughness Ra Value (micro-inch)	7-9	17-21	28-30
Surface Haze (%) (ASTM D1003)	0.8	5-7	17.3
Peel Seal Strength (Newton/15 mm) Before Autoclaving	28-30	18-20	6-6.5
Peel Seal Strength (Newton/15 mm) After Autoclaving	29-32	18-19	6-7

[0115] While the specific embodiment has been illustrated and described, numerous modifications come to mind without significantly departing from the spirit of the invention and the scope of protection is only limited by the scope of the accompanying Claims.

We claim:

1. A polymer blend comprising:

a first component of a polymeric material capable of being cross-linked and selected from the group consisting of an ethylene containing polymer, the first component present in an amount by weight of the blend from about 50% to about 95%, the first component having a first melting point temperature determined by DSC;

a second component not readily cross-linkable and selected from the group consisting of propylene-containing polymers and methyl-pentene-containing polymers, the second component being present in an amount by weight of the blend from about 50% to about

5%, the second component having a second melting point temperature determined by DSC; and

a portion of the first component being cross-linked and the second component is essentially free of cross-linking.

2. The blend of claim 1, wherein the second melting point temperature is higher than the first melting point temperature.

3. The blend of claim 2 when formed into a film the film is capable of forming a peel seal to itself when heated to below the second melting point temperature.

4. The blend of claim 2 is capable of forming a peel seal to itself when heated to above the first melting point temperature but below the second melting point temperature.

5. The blend of claim 3 when formed into a film the film is capable of forming a permanent seal to itself when heated to above the second melting point temperature.

6. The blend of claim 1 is capable of being sterilized by steam at a temperature from about 100° C. to about 130° C.

7. The blend of claim 2, wherein a peel seal heat sealing window is defined between a range of temperatures existing between the first melting point temperature and the second melting point temperature.

8. The blend of claim 7, wherein the peel seal heat sealing window includes at least one temperature point within a range of temperatures suitable for steam sterilization.

9. The blend of claim 7, wherein the peel seal window includes at least one temperature point within the range of from about 75° C. to about 135° C.

10. The blend of claim 1, wherein the ethylene-containing polymer is selected from the group consisting of: ethylene homopolymers, and ethylene copolymers.

11. The blend of claim 10, wherein the ethylene copolymer is obtained by reacting ethylene with a comonomer selected from the group consisting of: α -olefins, vinyl esters, vinyl carboxylic acids, alkyl substituted vinyl esters, alkyl substituted vinyl carboxylic acids, acrylic acids, ester derivatives of acrylic acids, alkyl substituted acrylic acids, ester derivatives of alkyl substituted acrylic acids and ion stabilized alkyl substituted acrylic acids.

12. The blend of claim 11, wherein the ethylene and α -olefin copolymer has a density of less than about 0.915 g/cc

13. The blend of claim 12, wherein the ethylene copolymer is obtained using a single-site catalyst.

14. The blend of claim 1, wherein the propylene containing polymer is selected from the group consisting of propylene homopolymers and propylene copolymers.

15. The blend of claim 14, wherein the propylene containing polymer has a modulus of elasticity of less than about 200,000 psi.

16. The blend of claim 1, wherein the methylpentene-containing polymer is selected from the group consisting of: homopolymers of 4-methylpentene-1, and copolymers of 4-methylpentene-1.

17. The blend of claim 1, wherein the first component is present in an amount by weight of from about 55% to about 90%.

18. The blend of claim 1, wherein the first component is present in an amount by weight of from about 60% to about 80%.

19. The blend of claim 1, wherein the first component is present in an amount by weight of from about 65% to about 75%.

20. The blend of claim 1, wherein the first component is a blend of ethylene containing polymers.

21. The blend of claim 1, wherein the second component is a blend selected from the group consisting of at least one propylene-containing polymer, at least one methyl-pentene-containing polymer, and at least one propylene-containing polymer and at least one methyl-pentene-containing polymer.

22. A monolayer film comprising:

a polymer blend of a first component of a polymeric material capable of being cross-linked and selected from the group consisting of an ethylene containing polymer, the first component present in an amount by weight of the film from about 50% to about 95%, the first component having a first melting point temperature determined by DSC, a second component not readily cross-linkable and selected from the group consisting of propylene containing polymers and methyl pentene containing polymers, the second component being present in an amount by weight of the film from about 50% to about 5%, the second component having a second melting point temperature determined by DSC; and a portion of the first component being cross-linked and the second component is essentially free of cross-linking.

23. The film of claim 22, wherein the second melting point temperature is higher than the first melting point temperature.

24. The film of claim 22 is capable of forming a peel seal to itself when heated to above the first melting point temperature but below the second melting point temperature.

25. The film of claim 24 is capable of forming a permanent seal to itself when heated above the second melting point temperature.

26. The film of claim 22 is capable of being sterilized by steam at a temperature from about 100° C. to about 130° C.

27. The film of claim 23, wherein a peel seal heat sealing window is defined between a range of temperatures existing between the first melting point temperature and the second melting point temperature.

28. The film of claim 27, wherein the peel seal heat sealing window includes at least one temperature point within a range of temperatures suitable for steam sterilization.

29. The film of claim 27, wherein the peel seal heat sealing window includes at least one temperature point within the range of from about 75° C. to about 135° C.

30. The film of claim 22 is capable of forming a peel seal with itself that is capable of adhesive release.

31. The film of claim 22, wherein the ethylene containing polymer is selected from the group consisting of: ethylene homopolymers, and ethylene copolymers.

32. The film of claim 31, wherein the ethylene copolymer is obtained by reacting ethylene with a comonomer selected from the group consisting of: α -olefins, vinyl esters, vinyl carboxylic acids, alkyl substituted vinyl esters, alkyl substituted vinyl carboxylic acids, acrylic acids, ester derivatives of acrylic acids, alkyl substituted acrylic acids, ester derivatives of alkyl substituted acrylic acids and ion stabilized alkyl substituted acrylic acids.

33. The film of claim 32, wherein the ethylene and α -olefin copolymer has a density of less than about 0.915 g/cc.

34. The film of claim 33, wherein the ethylene copolymer is obtained using a single-site catalyst.

35. The film of claim 22, wherein the propylene-containing polymer is selected from the group consisting of propylene homopolymers and propylene copolymers.

36. The film of claim 22, wherein the methylpentene-containing polymer is selected from the group consisting of: homopolymers of 4-methylpentene-1, and copolymers of 4-methylpentene-1.

37. The film of claim 35, wherein the propylene containing polymer has a modulus of elasticity of less than about 200,000 psi.

38. The film of claim 22, wherein the first component is a blend of ethylene containing polymers.

39. The film of claim 22, wherein the second component is a blend selected from the group consisting of at least one propylene-containing polymer, at least one methyl-pentene-containing polymer, and at least one propylene-containing polymer and at least one methyl-pentene-containing polymer.

40. A multiple layered film comprising:

a first layer of a first polymer blend of a first component of a polymeric material capable of being cross-linked and selected from the group consisting of an ethylene containing polymer, the first component present in an amount by weight of the blend from about 50% to about 95%, the first component having a first melting point temperature determined by DSC, a second component not readily cross-linkable and selected from the group consisting of propylene containing polymers and methyl-pentene containing polymers, the second component being present in an amount by weight of the blend from about 50% to about 5%, the second component having a second melting point temperature determined by DSC; and a portion of the first component being cross-linked and the second component is essentially free of cross-linking; and

a second layer attached to the first layer and being of a polymer, paper, or metal foil.

41. The film of claim 40, wherein the second melting point temperature is higher than the first melting point temperature.

42. The film of claim 40 is capable of forming a peel seal to itself when heated to above the first melting point temperature but below the second melting point temperature.

43. The film of claim 42 is capable of forming a permanent seal to itself when heated to above the second melting point temperature.

44. The film of claim 40 is capable of being sterilized by steam at a temperature from about 100° C. to about 130° C.

45. The film of claim 40, wherein a peel seal window is defined between a range of temperatures existing between the first melting point temperature and the second melting point temperature.

46. The film of claim 45, wherein the peel seal window includes at least one temperature point within a range of temperatures suitable for steam sterilization.

47. The film of claim 45, wherein the peel seal heat sealing window includes at least one temperature point within the range of from about 75° C. to about 135° C.

48. The film of claim 40 is capable of forming a peel seal with itself that is capable of adhesive release.

49. The film of claim 40, wherein the ethylene containing polymer is selected from the group consisting of: ethylene homopolymers, and ethylene copolymers.

50. The film of claim 49, wherein the ethylene copolymer is obtained by reacting ethylene with a comonomer selected from the group consisting of: α -olefins, vinyl esters, vinyl carboxylic acids, alkyl substituted vinyl esters, alkyl substituted vinyl carboxylic acids, acrylic acids, ester derivatives of acrylic acids, alkyl substituted acrylic acids, ester derivatives of alkyl substituted acrylic acids and ion stabilized alkyl substituted acrylic acids.

51. The film of claim 40, wherein the ethylene and α -olefin copolymer has a density of less than about 0.915 g/cc.

52. The film of claim 40, wherein the ethylene copolymer is obtained using a single-site catalyst.

53. The film of claim 40, wherein the propylene-containing polymer is selected from the group consisting of propylene homopolymers and propylene copolymers.

54. The film of claim 53, wherein the propylene containing polymer has a modulus of elasticity of less than about 200,000 psi.

55. The film of claim 40, wherein the methylpentene-containing polymer is selected from the group consisting of: homopolymers of 4-methylpentene-1, and copolymers of 4-methylpentene-1.

56. The film of claim 40, wherein the first component is a blend of ethylene containing polymers.

57. The film of claim 40, wherein the second component is a blend selected from the group consisting of at least one propylene containing polymer, at least one methyl-pentene-containing polymer, and at least one propylene containing polymer with at least one methyl-pentene-containing polymer.

58. The film of claim 40, further comprising a third layer attached to the second layer opposite the first layer.

59. The film of claim 58, wherein the third layer is of a second polymer blend.

60. The film of claim 59, wherein the second polymer blend comprises a third component of a polymeric material capable of being cross-linked and selected from the group consisting of an ethylene containing polymer, the third component present in an amount by weight of the blend from about 50% to about 95%, the third component having a third melting point temperature determined by DSC, a fourth component not readily cross-linkable and selected from the group consisting of propylene containing polymers and methyl pentene containing polymers, the fourth component being present in an amount by weight of the blend from about 50% to about 5%, the fourth component having a fourth melting point temperature determined by DSC; and a portion of the third component being cross-linked and the fourth component is essentially free of cross-linking.

61. A tubing comprising:

a sidewall of a polymer blend of a first component of a polymeric material capable of being cross-linked and selected from the group consisting of an ethylene containing polymer, the first component present in an amount by weight of the blend from about 50% to about 95%, the first component having a first melting point temperature determined by DSC, a second component not readily cross-linkable and selected from the group consisting of propylene containing polymers and methyl-pentene containing polymers, the second com-

ponent being present in an amount by weight of the blend from about 50% to about 5%, the second component having a second melting point temperature determined by DSC; and a portion of the first component being cross-linked and the second component is essentially free of cross-linking.

62. The tubing of claim 61, wherein the second melting point temperature is higher than the first melting point temperature.

63. The tubing of claim 61 is capable of forming a peel seal to itself when heated to a temperature below the second melting point temperature.

64. The tubing of claim 63 is capable of forming a permanent seal to itself when heated to above the second melting point temperature.

65. The tubing of claim 61, wherein a peel seal heat sealing window is defined between the first melting point temperature and the second melting point temperature.

66. The tubing of claim 65, wherein the peel seal heat sealing window includes at least one temperature within the range of from about 75° C. to about 135° C.

67. The tubing of claim 65, wherein the peel seal heat sealing window includes at least one temperature point within a range of temperatures suitable for steam sterilization.

68. The tubing of claim 67, wherein the peel seal window includes at least one temperature point within the range of from about 100° C. to about 130° C.

69. The tubing of claim 61 is capable of forming a peel seal with itself that is capable of adhesive release.

70. The tubing of claim 61, wherein the ethylene containing polymer is selected from the group consisting of: ethylene homopolymers, and ethylene copolymers.

71. The tubing of claim 70, wherein the ethylene copolymer is obtained by reacting ethylene with a comonomer selected from the group consisting of: α -olefins, vinyl esters, vinyl carboxylic acids, alkyl substituted vinyl esters, alkyl substituted vinyl carboxylic acids, acrylic acids, ester derivatives of acrylic acids, alkyl substituted acrylic acids, ester derivatives of alkyl substituted acrylic acids and ion stabilized alkyl substituted acrylic acids.

72. The tubing of claim 71, wherein the ethylene and α -olefin copolymer has a density of less than about 0.915 g/cc.

73. The tubing of claim 70, wherein the ethylene copolymer is obtained using a single-site catalyst.

74. The tubing of claim 61, wherein the propylene containing polymer is selected from the group consisting of propylene homopolymers and propylene copolymers.

75. The tubing of claim 74, wherein the propylene containing polymer has a modulus of elasticity of less than about 200,000 psi.

76. The tubing of claim 61, wherein the methylpentene-containing polymer is selected from the group consisting of: homopolymers of 4-methylpentene-1, and copolymers of 4-methylpentene-1.

77. The tubing of claim 61, wherein the first component is a blend of ethylene containing polymers.

78. The tubing of claim 61, wherein the second component is a blend selected from the group containing of at least one propylene containing polymer, at least one methylpentene containing polymer, and at least one propylene containing polymer with at least one methylpentene-containing polymer.

79. A flowable materials container comprising:

a first sidewall of a first polymer blend of a first component of a polymeric material capable of being cross-linked and selected from the group consisting of an ethylene-containing polymer, the first component present in an amount by weight of the first blend from about 50% to about 95%, the first component having a first melting point temperature determined by DSC, a second component not readily cross-linkable and selected from the group consisting of propylene containing polymers and methyl-pentene containing polymers, the second component being present in an amount by weight of the first blend from about 50% to about 5%, the second component having a second melting point temperature determined by DSC; and a portion of the first component being cross-linked and the second component is essentially free of cross-linking; and

a second sidewall attached to the first sidewall along a peripheral seam to define a chamber between the first sidewall and the second sidewall, the second sidewall being of a polymer, a paper or a metal foil.

80. The container of claim 79, wherein the second sidewall is of a second polymer blend.

81. The container of claim 80, wherein the second polymer blend is the same as the first polymer blend.

82. The container of claim 79, further comprising a peel seal between the first sidewall and the second sidewall.

83. The container of claim 82, wherein the peel seal separates the chamber into a first sub-chamber and a second sub-chamber.

84. The container of claim 82, wherein the peel seal is capable of adhesive release.

85. The container of claim 82, wherein the peel seal extends between lateral edges of the container.

86. The container of claim 82, wherein the peel seal extends between longitudinal edges of the container.

87. The container of claim 82, wherein the peripheral seam is a permanent seal.

88. The container of claim 82, wherein the peel seal is formed by heating the first sidewall to above the first melting point temperature but below the second melting point temperature.

89. The container film of claim 88, wherein the permanent seal is formed by heating the first sidewall to above the second melting point temperature.

90. The container of claim 79 is capable of being sterilized by steam at a temperature from about 100° C. to about 130° C.

91. The container of claim 79, wherein the second melting point temperature is higher than the first melting point temperature, and wherein a peel seal heat sealing window is defined between a range of temperatures existing between the first melting point temperature and the second melting point temperature.

92. The container of claim 91, wherein the peel seal heat sealing window includes at least one temperature point within a range of temperatures suitable for steam sterilization.

93. The container of claim 91, wherein the peel seal heat sealing window includes at least one temperature point within the range of from about 75° C. to about 135° C.

94. The container of claim 79, wherein the ethylene-containing polymer is selected from the group consisting of: ethylene homopolymers, and ethylene copolymers.

95. The container of claim 94, wherein the ethylene copolymer is obtained by reacting ethylene with a comonomer selected from the group consisting of: α -olefins, vinyl esters, vinyl carboxylic acids, alkyl substituted vinyl esters, alkyl substituted vinyl carboxylic acids, acrylic acids, ester derivatives of acrylic acids, alkyl substituted acrylic acids, ester derivatives of alkyl substituted acrylic acids and ion stabilized alkyl substituted acrylic acids.

96. The container of claim 95, wherein the ethylene and α -olefin copolymer has a density of less than about 0.915 g/cc.

97. The container of claim 96, wherein the ethylene copolymer is obtained using a single-site catalyst.

98. The container of claim 79, wherein the propylene-containing polymer is selected from the group consisting of propylene homopolymers and propylene copolymers.

99. The container of claim 98, wherein the propylene-containing polymer has a modulus of elasticity of less than about 200,000 psi.

100. The container of claim 98, wherein the methylpentene-containing polymer is selected from the group consisting of: homopolymers of 4-methylpentene-1, and copolymers of 4-methylpentene-1.

101. The container of claim 79, wherein the first component is a blend of ethylene containing polymers.

102. The container of claim 79, wherein the second component is a blend selected from the group consisting of at least one propylene-containing polymer, at least one methyl-pentene containing polymer, and at least one propylene-containing polymer with at least one methylpentene-containing polymer.

103. A multichamber flowable materials container comprising:

- a first sidewall of a first polymer blend of a first component of a polymeric material capable of being cross-linked and selected from the group consisting of an ethylene-containing polymer, the first component present in an amount by weight of the first blend from about 50% to about 95%, the first component having a first melting point determined by DSC, a second component not readily cross-linkable and selected from the group consisting of propylene containing polymers and methyl pentene containing polymers, the second component being present in an amount by weight of the first blend from about 50% to about 5%, the second component having a second melting point temperature determined by DSC; and a portion of the first component being cross-linked and the second component is essentially free of cross-linking;

- a second sidewall attached to the first sidewall along a peripheral seam to define a chamber between the first sidewall and the second sidewall, the second sidewall being of a polymer, a paper or a metal foil; and

- a peelable seal between the first sidewall and the second sidewall and dividing the chamber into two subchambers.

104. The container of claim 103, wherein the peelable seal is capable of an adhesive release.

105. The container of claim 103, wherein the peelable seal is capable of being separated with a force of greater than about 3 N/15 mm.

106. The container of claim 103, wherein the container is capable of being steam sterilized.

107. The container of claim 106, wherein the peel seal has substantially the same strength when comparing the strength of the peel seal before the container is steam sterilized with the strength of the peel seal after the container is steam sterilized.

108. The container of claim 107, wherein the strength of the peel seal before steam sterilization and after steam sterilization varies by less than 30%.

109. The container of claim 107, wherein the strength of the peel seal before steam sterilization and after steam sterilization varies by less than 20%.

110. The container of claim 107, wherein the strength of the peel seal before steam sterilization and after steam sterilization varies by less than 10%.

111. A method for forming a film comprising the steps of:

- providing a polymer blend of a first component of a polymeric material capable of being cross-linked and selected from the group consisting of an ethylene-containing polymer, the first component present in an amount by weight of the blend from about 50% to about 95%, the first component having a first melting point temperature determined by DSC, a second component not readily cross-linkable and selected from the group consisting of propylene containing polymers and methyl pentene containing polymers, the second component being present in an amount by weight of the blend from about 50% to about 5%, the second component having a second melting point temperature determined by DSC;

- forming the polymer blend into a film; and

- cross-linking the first component while the second component is essentially free of cross-linking.

112. The method of claim 111, wherein the step of forming comprises a polymer processing technique selected from the group consisting of extrusion, blown extrusion, thermoforming, calendaring, compression molding and blow molding.

113. The method of claim 111, wherein the film is a monolayer film.

114. The method of claim 111, wherein the film is a multiple-layer film.

115. A method for forming a multiple-chamber container comprising the steps of:

- providing a first film of a polymer blend of a first component of a polymeric material capable of being cross-linked and selected from the group consisting of an ethylene-containing polymer, the first component present in an amount by weight of the blend from about 50% to about 95%, the first component having a first melting point temperature determined by DSC, a second component not readily cross-linkable and selected from the group consisting of propylene containing polymers and methyl pentene containing polymers, the second component being present in an amount by weight of the blend from about 50% to about 5%, the second component having a second melting point tem-

perature determined by DSC, the second melting point temperature being higher than the first melting point temperature;

providing a second film of a polymeric material, paper or metal foil;

cross-linking the first component while the second component is essentially free of cross-linking;

positioning the first film into registration with the second film;

sealing a first portion of the first film to the second film to form a permanent seal; and

sealing a second portion of the first film to the second film to form a peel seal.

116. The method of claim 115, wherein the step of sealing the first portion comprises the steps of sealing about a peripheral portion of the first film and the second film to define a chamber.

117. The method of claim 116, wherein the step of sealing about a peripheral portion of the first film comprises the step of heating the first film to a temperature higher than the second melting point temperature.

118. The method of claim 115, wherein the peel seal divides the chamber into two subchambers.

119. The method of claim 115, wherein the step of sealing a second portion of the first film to the second film to define a peel seal comprises the step of heating the first film to a temperature higher than the first melting point temperature but less than the second melting point temperature.

120. The method of claim 115, wherein a peel seal heat sealing window is defined between the first melting point temperature and the second melting point temperature, wherein the step of sealing a second portion of the first film to the second film to define a peel seal comprises the step of heating the first film to a temperature within the peel seal window.

121. The method of claim 120, wherein the peel seal heat sealing window includes temperatures from about 75° C. to about 135° C.

122. The method of claim 115, wherein the step of cross-linking comprises the step of exposing the first film to a chemical cross-linking agent or to a radiation cross-linking source or to both a chemical cross-linking agent and a radiation cross-linking source.

123. The method of claim 122, wherein the chemical cross-linking agent is selected from the group consisting of: peroxides, silanes, sulfur, and multifunctional acrylates.

124. The method of claim 122, wherein the radiation cross-linking source is selected from the group consisting of: ultra-violet light, electron beam, and gamma rays.

125. The method of claim 115, wherein the step of forming a permanent seal is carried out before the step of forming the peel seal.

126. The method of claim 115, wherein the step of forming a permanent seal is carried out after the step of forming the peel seal.

127. The method of claim 115, wherein the cross-linking step is carried out before the step of sealing a first portion of film.

128. The method of claim 115, wherein the step of forming a permanent seal is carried out simultaneously with the step of forming the peel seal.

129. A multichamber flowable materials container comprising:

a first sidewall of a first polymer blend of a first component of a polymeric material capable of being cross-linked and selected from the group consisting of an ethylene-containing polymer, the first component present in an amount by weight of the first blend from about 50% to about 95%, the first component having a first melting point temperature determined by DSC, a second component not readily cross-linkable and selected from the group consisting of propylene containing polymers and methyl-pentene-containing polymers, the second component being present in an amount by weight of the first blend from about 50% to about 5%, the second component having a second melting point temperature determined by DSC; and a portion of the first component being cross-linked and the second component is essentially free of cross-linking;

a second sidewall attached to the first sidewall along a peripheral seam to define a chamber between the first sidewall and the second sidewall, the second sidewall being of a polymer, a paper or a metal foil;

a peelable seal between the first sidewall and the second sidewall and dividing the chamber into two subchambers; and

wherein the peelable seal can be opened by applying a force to the container and wherein the force remains essentially constant when comparing the peelable seal of the container before the container has been autoclaved and after the container has been autoclaved.

130. The container of claim 129, wherein the force required to open the peelable seal prior to the autoclave process and after the autoclave process varies by less than 30%.

131. The container of claim 129, wherein the force required to open the peelable seal prior to the autoclave process and after the autoclave process varies by less than 20%.

132. The container of claim 129, wherein the force required to open the peelable seal prior to the autoclave process and after the autoclave process varies by less than 10%.

133. The container of claim 132, wherein the peelable seal is capable of being separated with a force of greater than about 3 N/15 mm.

134. The container of claim 129 wherein a range of temperatures extends between the first melting point temperature and the second melting point temperature to define a peel seal heat sealing window.

135. The container of claim 134 wherein the peelable seal strength remains essentially constant when sealed within the peel seal heat sealing window.

136. A layered structure comprising:

a first layer and a second layer of a material not capable of forming a peel seal; and

a third layer of a material capable of forming a peel seal interposed between the first layer and the second layer to form a peel seal between the first layer and the second layer.

137. A method for forming a textured film comprising the steps of:

providing a polymer blend of a first component of a polymeric material capable of being cross-linked and selected from the group consisting of an ethylene-containing polymer, the first component present in an amount by weight of the blend from about 50% to about 95%, the first component having a first melting point temperature determined by DSC, a second component not readily cross-linkable and selected from the group consisting of propylene containing polymers and methyl pentene containing polymers, the second component being present in an amount by weight of the blend from about 50% to about 5%, the second component having a second melting point temperature determined by DSC;

forming the polymer blend into a film;

imparting a textured surface on the film; and

cross-linking the first component while the second component is essentially free of cross-linking.

138. The method of claim 137 wherein the step of imparting a textured surface on the film comprises the step of extruding the film.

139. The method of claim 137 wherein the step of extruding the film includes the step of running the film in contact with a textured roller.

140. The method of claim 137 wherein a peel seal heat sealing window is defined between the first melting point temperature and the second melting point temperature, the method further comprising the steps of:

placing a portion of the film in registration with another portion of the film to define an overlap area;

heating the overlap area to a temperature within the peel seal heat sealing window to define a peel seal.

141. The method of claim 140 wherein the peel seal has a strength that remains essentially constant when sealed within the peel seal heat sealing window.

142. The method of claim 140 wherein the peel seal has a strength that remains essentially constant when comparing the film before being autoclaved and after being autoclaved.

143. The method of claim 140 wherein the surface texture can be measured by haze values and wherein as the haze values increase the peel seal strength decreases.

144. The method of claim 140 wherein the surface texture can be measured by surface roughness values and wherein as the surface roughness values increase the peel seal strength decreases.

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EXHIBIT D

United States Patent [19]

Hamilton et al.

[11] Patent Number: 5,397,842

[45] Date of Patent: Mar. 14, 1995

[54] **POLYOLEFIN/SEGMENTED COPOLYMER BLEND AND PROCESS**

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[51] Int. Cl.⁶ C08F 255/02

[52] U.S. Cl. 525/263; 525/265; 525/285; 525/279; 525/302; 525/309

[58] Field of Search 525/75, 70, 95, 263, 525/265, 279, 285, 302

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[57] ABSTRACT

A blend of a polyolefin, such as polypropylene, with a segmented copolymer containing both polyolefin segments and segments derived from greater than 20 to about 100% of a vinyl aromatic monomer is useful in applications where high melt strength is desired.

2 Claims, No Drawings

POLYOLEFIN/SEGMENTED COPOLYMER BLEND AND PROCESS

This application is a continuation-in-part of U.S. application Ser. No. 07/747,555, filed Aug. 20, 1991, now abandoned.

FIELD OF THE INVENTION

This invention relates broadly to a novel blend of a segmented copolymer and a polyolefin, the blend having high resistance to sagging without increasing melt viscosity, and to a method of making the same.

More particularly, the invention relates to a polymerized monoolefin having grafted thereto, by covalent bonding, a polymeric vinyl monomer chain having vinyl aromatic monomer units.

The invention further relates to a process wherein to the non-polar polyolefin, preferably polypropylene or polyethylene, is added a vinyl aromatic monomer which is to be grafted to the polyolefin such as styrene, methylstyrene, and the like, or mixtures of these with methyl methacrylate and/or butyl acrylate. An initiator is introduced with the monomer either in admixture or in separate feeds. The initiator may also be introduced after the monomer is introduced. The initiator has a one hour half life between about 110° to about 125° C. The vinyl monomer may act like a solvent to swell the polyolefin. Heating of this mixture may cause the polyolefin to become completely swollen, but there need be no equilibrium swelling reached prior to polymerization. Further heating will cause the grafting, reaction to begin. An exothermic reaction occurs. The graft polymer is then blended with one or more suitable polyolefins such as polypropylene or polyethylene, and extruded or otherwise processed into a desired shape, which (for selected segmented copolymers) may be thermoformed with good resistance to sag.

BACKGROUND OF THE INVENTION

Non-polar polyolefins, especially polypropylene and polyethylene and mixtures in various low-density, high-density, and linear low-density form, are major articles of commerce for a wide variety of uses. Nevertheless, there exist specialty needs for which the marketplace has not provided a satisfactory answer. Among these are to overcome the difficulty of thermoforming and processing of the polyolefin, especially untitled, in a molten or semi-molten form (substantially above its melting point); the polymer tends to sag readily under its own weight because it exhibits an undesirably low stiffness, and to form shapes of grossly non-uniform thicknesses upon thermoforming. Attempts to correct this by increasing the molecular weight lead to difficulties in processing the higher molecular weight polymer not encountered with lower molecular weight polymers.

It is an object of this invention to provide blends of the segmented copolymer with a polyolefin matrix which exhibit improved physical performance in the melt, upon cooling, and in the solid state.

Further objects and advantages of this invention will appear as this specification progresses.

SUMMARY OF THE INVENTION

Broadly, the aforesaid objects and advantages are accomplished by copolymerizing onto a non-polar polyolefin trunk, at least one chain of a polymerized

vinyl monomer present in a weight ratio with the polyolefin of from about 1:20 to 4:1. In the present invention, polyolefin refers to polymers derived from the polymerization or copolymerization of monoethylenically unsaturated olefins, such as ethylene, propylene, butene-1, and the like. Segmented copolymers containing blocks whose formal structure is that of a polyolefin, but where the block component is not formed by the direct polymerization (such as Ziegler-Natta catalyzed polymerization) of a monoolefin, are unsatisfactory for improving the melt strength of polyolefins.

The segmented copolymer is derived from above 20% of a vinyl aromatic monomer and up to less than 80%, preferably less than about 60%, and most preferably less than 20% based on the total monomer weight, of one or more monomers copolymerizable with the vinyl aromatic monomer such as another vinyl aromatic monomer, substituted and unsubstituted acrylates, methacrylates, acrylic acids, methacrylic acids and anhydrides, for example, maleic anhydride. By "segmented" we mean that the copolymer can be a graft copolymer or a block copolymer or a combination of a graft copolymer and a block copolymer. In one method of manufacturing, when a segmented copolymer is prepared from a polyolefin in solution (for example in tert-butyl benzene), the vinyl monomers are added to the polyolefin together with an initiator which generates a constant low radical concentration, or radical "flux", at the solution temperature. These radicals initiate polymerization of the monomer and cause formation of a covalent bond with the trunk.

A unique aspect of the present invention lies in the discovery that the segmented copolymers of polyolefins and polymers formed from vinyl aromatic monomers impart improved melt strength to polyolefins only when prepared under certain specified conditions, which appear to be related to the half-life of the free-radical initiator employed in their preparation. More specifically, a free-radical initiator should be employed which has a half-life of one hour within the temperature range of about 110 to about 125 degrees C. Employment of initiators with half-lives of one hour realized at temperatures outside this range produces segmented copolymers in high efficiency, but those segmented copolymers are much less effective in improving the sag resistance when combined with polyolefins. Although tested most thoroughly with the non-solvent process described herein, the process restriction is applicable to solution and aqueous heterogenous processes also. Unlike the grafting process described for methacrylic monomers in U.S. Pat. No. 4,957,974, wherein the radical flux during polymerization was important to achieving an additive which improved the melt strength of polyolefins, for processes involving vinyl aromatic monomers, the radical flux per se does not seem to be critical.

The resulting segmented copolymer (which may include ungrafted homopolymers) may be blended with polyolefin either as a result of the manner by which it is made, or after it is made. The resulting blend may be extruded into a desired shape either directly, or after pelletization. The resulting blended product exhibits high sag resistance without an increase in melt viscosity, as compared with similar ungrafted polymers, viz.: polyolefins without a high molecular weight chain or chains covalently bonded thereto.

The segmented copolymer may also be blended with polymers other than polyolefins, and particularly with mixtures of two or more polymers which are poorly

compatible with one another, and which may or may not include polyolefins, to improve the compatibility of the resulting mixture.

One process for making the blends of this invention involves admixing the polyolefin, the vinyl aromatic monomer and an initiator, and heating to above 100° C. but below the softening point of the polyolefin (to about 140° C. in the case of polypropylene) to decompose the initiator to begin the grafting reaction. The radicals initiate polymerization of the monomer and formation of a covalent bond therewith on the polyolefin trunk. The resultant product consists of the polyolefin with the chain grafted thereto, unreacted polymer, and ungrafted polyvinyl monomer (the amount of which is small, as the grafting efficiency is high). The product may be directly blended with the polyolefin (since the process directly yields pellets). In this preferred method, it is believed a graft copolymer is formed by abstraction of a hydrogen atom from the polyolefin and polymerization of the monomer at that site. However, the possibility of some chain scission of the polyolefin to create polymerization sites at chain ends, and thus to form block copolymers, cannot be overlooked.

The product from the solution process may be pelletized, blended with another polyolefin and extruded into desired shape. Alternatively the reaction mixture may be extruded directly in a devolatilizing extruder to volatilize residual monomer, and thereafter blended with a polyolefin and the blend extruded to form article in such forms as sheets, tubes and the like.

DETAILED DESCRIPTION

In general this invention relates to a polymer blend comprising or consisting essentially of:

- a) a polyolefin and
- b) from about 0.1 to about 50% and preferably from 0.2 to less than about 10% of a segmented copolymer of a non-polar polyolefin (for example a polymer or copolymer of polyethylene, polypropylene, polybutylene, or poly(4-methylpentene)), covalently bonded to a polymer derived from greater than 20 to about 100% (preferably, from about 40 to about 100% and more preferably, from about 80 to about 100%) of a vinyl aromatic monomer such as styrene, methylstyrene, dimethylstyrene, ethylstyrene, isopropylstyrene, chlorostyrene, dichlorostyrene, trichlorostyrene, α -methylstyrene, bromostyrene, tribromostyrene, and the like and from about 0 to 80% (preferably from about 0 to about 60%, and more preferably from about 0 to about 20%) based on the total monomer weight, of one or more monomers copolymerizable with the vinyl aromatic monomer such as other vinyl aromatic monomers as defined above, substituted and unsubstituted acrylates and methacrylates, such as methyl methacrylate or lauryl methacrylate, N-vinyl pyrrolidone, acrylic acids, methacrylic acids and anhydrides such as maleic anhydride and the like. The copolymerizable monomer may also be a crosslinker containing at least two vinyl groups such as divinyl benzene, glycol dimethacrylate and the like.

The invention further relates to articles prepared from the above polymer blends, which articles may be in extruded, calendered, thermoformed or molded form, or which may be in the form of a fiber, sheet, or hollow container.

In the following, "LDPE" is low-density polyethylene, usually branched, of density of about 0.91 to about 0.94 g/cc; "HDPE" is high-density polyethylene of a density above about 0.95 g/cc; "LLDPE" is linear low-density polyethylene of density about 0.91 to about 0.95 g/cc; "EPDM" includes rubber terpolymers of ethylene, propylene, and a non-conjugated diene monomer, such as 1,4-hexadiene or ethyldienenorbornene.

The term "polar" or "non-polar" polymer, as used herein, is all relative to polyolefins. Generally "non-polar" means polymers which are predominantly formed from monomer units of mono- or di-olefins. "Polar", as generally understood in the polymer art, refers to monomers or polymers which contain an oxygen, nitrogen, or sulfur functionality. However, when compared to polyolefins other materials are also "polar" such as polystyrene. Methyl methacrylate, acrylonitrile, and vinyl phenyl sulfone are "polar" monomers, whereas polypropylene is a "non-polar" polymer.

The segmented copolymers to be added to the polyolefins to form the blends of this invention may be block or graft copolymers or a mixture of graft and block copolymers. The polymers to be modified in the grafting process include the non-polar olefin polymers and copolymers. Included are polypropylene, polyethylene (HDPE, LDPE, and LLDPE), polybutylene, ethylene-propylene copolymers at all ratios of ethylene and propylene, EPDM terpolymers at all ratios of ethylene and propylene and with diene monomer contents up to 10%, poly(l-butene), polymethylpentene, ethylene-vinyl acetate copolymers with vinyl acetate contents up to 25%, ethylene-methyl acrylate copolymers, ethylene-methyl methacrylate copolymers, and ethylene-ethyl acrylate copolymers. Also included are mixtures of these polymers in all ratios. Preferred is polypropylene or polyethylene.

A polyolefin trunk having a molecular weight of from about 200,000 to about 800,000 M_w (weight-average molecular weight) is especially preferred, but polyolefins having a molecular weight of about 50,000 to about 200,000 can be used with some beneficial effect. In general, a graft copolymer imparts greater melt-rheology improvement to a high-molecular-weight polyolefin.

Melt flow rate (mfr) is known to correlate with weight-average molecular weight. The preferred range of mfr values for the polyolefin trunks used in preparing the graft copolymers of the present invention are from about 20 to about 0.6 g/10 minutes as measured by ASTM Standard Method D-1238 (condition 230/2.16). The vinyl aromatic monomers that can be employed to prepare the vinyl polymers are preferably styrene type monomers such as styrene, methylstyrene, dimethylstyrene, ethylstyrene, α -methylstyrene, bromostyrene, chlorostyrene, and the like. Styrene is the most preferred.

Also, the preferred invention further relates to articles prepared from the polymer blends wherein the vinyl aromatic monomer is styrene, the polyolefin is polyethylene or polypropylene, preferably polypropylene, and the non-polar polyolefin component of the segmented copolymer is formed by the polymerization of ethylene or propylene, i.e., is polyethylene or polypropylene, preferably polypropylene. These articles may be in extruded, calendered, thermoformed or molded form, such as in the form of a fiber, sheet, or hollow container.

The initiators employed in the preferred swell process should preferably have a one hour half life at a temperature in the range of from about 110° C. to about 125° C. Such initiators include tert-butyl peroxybenzoate (125° C.), di-tert-butyl diperoxy phthalate (123° C.), tert-butyl peroxyacrylate (118° C.); 2,2 bis-tert-butyl(peroxybutane) (119° C.); tert-butylperoxy isopropyl carbonate (119° C.); 2,5 dimethyl-2,5-bis(benzoylperoxy)-hexane (118° C.); tert-butyl peracetate (120° C.); di-tert-butyl diperoxyphthalate (123° C.). The figures in parentheses are the 1 hr. half-life temperatures.

Other initiators may also be employed or example, 2,4-pentanedione peroxide (167° C.), di-tert-butyl peroxide (149° C.), 2,5-dimethyl-2,5-di(tert-butylperoxy)-hexyne (149° C.), and the like, to prepare segmented copolymers not useful as sag-resistance improvers. Such segmented copolymers can be utilized as compatibilizers for polyolefins blended with more polar resins.

The compounding portion of the thermoplastic polymer particles, vinyl aromatic monomer and polymerization initiator in the system prior to polymerization is

- (a) 50-99.9 weight parts, preferably 50-90 weight parts, of the thermoplastic polymer particles,
- (b) 50-0.1 weight parts, preferably 50-10 weight parts, of the vinyl monomer and
- (c) 0.05-20 weight parts, preferably 0.1-10 weight parts, of the polymerization initiator per 100 weight parts of the vinyl monomer.

A thermoplastic polymer particle content of less than the stated range (a vinyl monomer content greater than the range) results in agglomeration of the polymer particles during the reaction although multi-step addition of the monomers may be employed to avoid such agglomeration. A content of more than the stated range (a vinyl monomer content of less than the stated range) results in an inadequately modified product. A polymerization initiator content of less than the range cannot fully polymerize the vinyl monomer, whereas a greater content leads to reactions other than polymerization such as deterioration of the polymer or gelation.

A typical method for combining the thermoplastic polymer particles with a vinyl monomer involves mixing the thermoplastic polymer particles with the vinyl monomer containing the polymerization initiator (and other additives as required). Another method is by mixing the thermoplastic polymer particles with the polymerization initiator and then adding the vinyl monomer. Another method is by adding monomer and initiator throughout the reaction. Another method is by adding monomer, heating, and then adding initiator. Since combination of monomer, polymer, and initiator should be efficiently done by heating under conditions where the polymerization initiator is not decomposed, the temperature should ordinarily be less than 100° C., preferably about room temperature to 90° C. It is preferred for ease in handling the resultant product that, when polypropylene is used as the polymer particle, it be in a form with high surface; however, polyolefin pellets without enhanced surface area may be employed.

The combination time for admixture and heat-up is ordinarily on the order of from ½ to 8 hr. In mixing the thermoplastic polymer particles with a vinyl monomer (and polymerization initiator), auxiliary materials such as plasticizer, lubricant, crosslinker and the like may be simultaneously combined (these auxiliary materials may already have been added to the thermoplastic polymer particles or can be compounded after polymerization).

It has been found that with styrene, no additional impregnation time need be involved beyond that of heating the monomer and polymer to the desired temperature. Sufficient combination of monomer and polyolefin occurs during the mixing and heat-up cycle.

In order to control the molecular weight of the polymer produced by the polymerization of the vinyl monomer, a chain transfer agent such as n-butyl mercaptan, n-dodecyl mercaptan or tert-dodecyl mercaptan may be added.

By increasing the temperature of the impregnated thermoplastic polymer particles or of the well-mixed monomer/polyolefin combination obtained in the above-stated manner to a level at which the polymerization initiator is decomposed at a suitable rate, the impregnated or well-mixed vinyl monomer is polymerized to form the modified thermoplastic polymer particles.

Because radical polymerization is involved, heating should be done in an essentially oxygen-free atmosphere and suitable mixing provided during polymerization. Since it is essential to polymerize under conditions where the thermoplastic polymer particles are not dissolved or fused, the polymerizing temperature should be in the range of from about 60° to about 150° C. Exceeding 50° C. not only favors gelation but also melt fusion or aggregation of the particles.

The polymerizing time is ordinarily on the order of from 0.5 to about 10 hr and the polymerizing pressure ordinarily on the order of ordinary pressure to 10 kg/sq cm. The mixing, impregnating, and polymerizing processes are implemented preferably in the absence of water. One means employs of a single apparatus provided with means for heating and mixing without recourse to stirring vanes. In order to impregnate uniformly and distribute the heat evenly, it is desirable that the components of the system be continuously mixed throughout the impregnation and polymerization processes. Mixing by means of stirring vanes is undesirable because the thermoplastic polymer particles are often marred or fractured while the stirring may be inadequate. Mixing should be done by means of a self-moving apparatus without depending on vanes such as the self-rotating type, vibration type or self-rotating and vibration type unit. A unit may also be provided with a baffle plate for increasing the degree of mixing among others, a system in which the unit freely rotates on its own axis is desirable, especially a rotating axis that is set at an angle of less than 80 degrees with respect to the horizontal axis. Any unit having a horizontal axis of rotation which is commonly used is satisfactory. Heating methods involve the circulation of a suitable medium such as steam, hot water or oil or a means for providing electrical heat from within or without the unit may be used. After polymerization, even when simple drying or deodorization is required, post-processings such as ventilation and decompression can be done within the unit without recourse to other means.

Upon further study of the process, it has been found that reactors equipped with stirrers and with baffle or mixing vanes may be employed without as severe degradation of the resulting segmented copolymer's physical shape as had been first anticipated.

The process may be one shot, or when conducted in solution, run in a semicontinuous or continuous manner. Vinyl monomer and initiator may be added by means similar to those described above. Additives may also be added when the graft copolymer is blended with the matrix polymer. Such additives may include stabilizers

against light or heat, such as benzotriazoles, hindered amines, alkyl polysulfides such as dialkyl disulfides, and the like, lubricants, or plasticizers; flame retardants; and the like.

The product is isolated by stranding, cooling, chopping, drying, and bagging, or other known collection techniques. In the preferred one-shot process conducted without solvent, the product is already in pelletized form and need merely be collected.

The polyolefin and the graft copolymer may be blended by mixing the dry feed materials and extruding either directly to form a film, sheet or the like, or by collecting the blend and reprocessing it into the desired article, or by adding the polyolefin in the course of the devolatilization.

Polyolefins are often produced with one or more stabilizers to prevent degradation of the polymer appearance or physical properties during processing and/or end use. Such stabilizers may include metal salts such as metal stearates, which act as acid acceptors, hindered phenols, or phosphites which act as antioxidants, and sulfur-containing organic esters or derivatives, added as heat stabilizers. Examples of such additives, which are usually proprietary to the supplier, are metal stearates, 2,6-dimethylphenolic compounds, Ir-gafos 168 and thiodiesters of long-chain alcohols. Polyolefins may also contain light stabilizers, such as hindered amines, hydroxy benzotriazoles, and the like. All of the polyolefins used in the present examples are thought to contain small amounts of these proprietary stabilizers.

One way to specify the blend composition is that at least about 0.2% of the total formulation (polyolefin plus segmented copolymer) should be a chemically segmented polymer or copolymer within the molecular weight limits specified. The preferred maximum amount is about 10% grafted polymer, with up to about 5% segmented polymer being especially preferred for cost optimization and optimization of most properties of the blend.

Optionally, the blend of concentrate i.e., the segmented copolymer plus any ungrafted non-polar polyolefin or polymer of the vinyl aromatic monomer, and polyolefin, may be further modified by the introduction of fillers (both inorganic and organic), fibers, impact modifiers, colorants, stabilizers, flame retardants, and/or blowing agents.

Blowing agents may be gases, such as nitrogen or carbon dioxide, admixed with the polymer melt in the extruder and allowed to expand upon extrusion. More often, blowing agents are solids which liberate gases, usually nitrogen, at a specific melt temperature, and which are mixed into the melt, or blended from a pre-compounded mixture of the blowing agent dispersed in a polymeric matrix. The melt temperatures for the polyolefins are typically in the range of about 200° to about 230° C., although other temperatures may be used, depending on the specific blowing agent. Solid blowing agents include azo compounds such as azodicarbonamides, azoisobutyronitriles, hydroazo compounds, or compounds containing the nitroso group.

The processing of the polyolefin//segmented copolymer blend for improved sag resistance is performed in the melt. The sag resistance test described herein is an appropriate measure of achievement of the desired resistance, and is quantified by stating that acceptable and novel improvement of melt strength requires a sag slope value for the blend (which contains 5 weight percent of

segmented polymer, based on total content of polyolefin and segmented copolymer) below 20% of the value for the unmodified polypropylene under similar test conditions. This value converts to a melt strength ratio, defined as

$$\frac{\text{sag resistance of matrix polymer}}{\text{sag resistance of blend containing 5\% of segmented copolymer}}$$

of at least 5.

The blend of the segmented copolymer and polyolefin is useful in thermoforming, especially of large objects which sag prior to thermoforming, such as containers, cups, panels and the like. Thermoforming of polypropylene, including a list of commercial uses and a description of test methods, such as sag testing, is described in J. L. Thorne, "Thermoforming", Munich/Vienna/New York (1987). The blend is also useful in film making (especially blowing and extruding), blow molding, such as for forming drums, coolers industrial parts, automotive parts, and the like, fiber spinning, acid and basic dyeing, foaming, extrusion (sheet, pipe, and profile), coextrusion (multilayer film, sheet, preforms, and parisons, with or without the use of tie layers), hot melt adhesives, calendering, and extrusion coating (for the preparation of polymer/fabric, carpet, foil, and other multilayer constructions). Such graft copolymers, especially with small amounts of copolymerized acid functionality, are useful when blended with polyolefins for improved printability. The grafts themselves may be used as tie layers between otherwise incompatible polymers.

In extrusion, the copolymer is useful, especially with LLDPE, at reduction of melt fracture without an effect on the melt flow rate.

When polypropylene is modified with the copolymers of the present invention, it may be employed in the manufacture of many useful objects, such as extrusion- or injection-blown bottles for packaging of foodstuffs, aqueous solutions such as intravenous feeds, hot-filled items such as ketchup, or extruded articles in profile form such as clips, scrapers, window and door casings and the like. The foamed articles may be used as substitutes for wood in moldings, for packaging materials, for insulation or sound-deadening materials, for food containers, and other rigid-article applications. Films may be used in many protective or wrapping applications, such as for food packaging, blister packaging of consumer goods, and the like.

The copolymers of the present invention are useful in preparing polyolefin fibers, especially polypropylene fibers; they are especially useful when the graft copolymer is formed from a polypropylene trunk. Polypropylene is relatively easy to process into fibers having high strength and toughness.

Polypropylene fibers show certain deficiencies which include difficulty in dyeing and poor long-term dimensional stability. Grafts containing functional sites capable of accepting dye may be prepared by the present process by incorporating low levels of dye-accepting monomers, such as methacrylic acid, dimethylaminoethyl methacrylate, N-vinylpyridine, and the like. The improved sag resistance noted for the present segmented polymers in a polypropylene matrix should correspond to improvements in creep resistance of the fiber.

Polypropylene may be formed into fibers by slitting tape from extruded film to form large-denier, coarse

fibers, by extruding monofilaments into large-denier fibers with a controlled cross-sectional size, or by extruding multifilaments through a spinnerette to produce bundles of small-denier fibers. In all cases, the fibers may be draw-textured.

Polypropylene fibers may be used for, among other things, strapping, netting (including fish nets), slit tape, rope, twine, bags, carpet backing, foamed ribbon, upholstery, rugs, pond liners, awnings, swimming-pool covers, tarpaulins, lawn-furniture webbing, shades, bristles, sutures, cigarette filters, nonwoven fabrics, such as for tea bags, bed sheets, bandages, diaper liners and the like, and for doll hair, apparel and the like.

The copolymer of the present invention may also be used to improve the compatibility of polymers in blends where they would otherwise be poorly compatible. The segmented copolymer is incorporated into such blends, preferably at levels of from about 0.2 to about 10%, preferably from about 0.5 to about 5%, and more preferably from about 0.8 to about 2.5%, to achieve the desired improvement in compatibility. Higher levels of the segmented copolymer may be used, but increases above the preferred level generally show only small improvements in compatibility. For such blends, it is believed the segmented copolymers used as compatibilizers need not be only those which exhibit good sag resistance in polypropylene.

As noted above, compatibility is not easily predicted. As a general rule non-polar polymers are poorly compatible with more polar polymers, but poorly compatible blends may also be found experimentally among polar-polar or non-polar-non-polar blends. Examples of the non-polar polymers are olefinic polymers such as high- and low-density polyethylene and linear low-density polyethylene, polypropylene including atactic polypropylene, poly-1-butene, poly-iso-butylene, ethylene-propylene rubber, ethylene-acrylic acid copolymer, ethylene-propylenediene terpolymer rubber, ethylene-vinyl acetate copolymer, poly (ethylene-propylene), polymethylpentenes, and ionomers such as polymers of ethylene with metal-salt-neutralized acrylic acid.

Relatively more polar polymers, called "polar polymers" for the purposes of this disclosure, include acrylonitrile-butadiene-styrene polymer, acetal polymers, polyarylates, acrylic-styrene copolymers, acrylonitrile-styrene-acrylic polymers, acrylonitrile-styrene polymers modified with ethylene-propylene rubber, cellulose, polyester-polyether block copolymers, polyesters such as polybutylene terephthalate and polyethylene terephthalate, and including liquid-crystal polyesters, polyetheramides, polyetheretherketones, polyetherimides, polyethersulfones, ethylene-vinyl alcohol copolymers, polyvinyl chloride, chlorinated polyvinyl chloride, polyvinylidene chloride and fluoride, styrene polymers such as polystyrene, high-impact polystyrene, styrene-acrylonitrile copolymers, styrene-butadiene copolymers, styrene-maleic anhydride copolymers, alkyl-substituted styrenes copolymerized with styrene alone or with the additional monomers listed for styrene, polyphenylene ether, polyphenylene sulfide, polysulfone, polyurethane, polyamides, i.e., nylons such as nylon 6, nylon 6.6, nylon 6.9, nylon 6.10, nylon 6.12, nylon 11, nylon 12, amorphous nylons, polyamideimide, polycaprolactone, polyglutarimide, poly(methyl methacrylate); other C₁ to C₈ poly(alkyl (meth)acrylates) and polycarbonates. The acrylic polymers referred to above are polymers containing at least

50 weight percent, and preferably at least 80 weight percent, of mers of acrylic acid and/or methacrylic acid (referred to collectively as (meth)acrylic acid) or their esters, preferably their alkyl esters and more preferably their alkyl esters in which the alkyl group contains from one to eight, preferably one to four, carbon atoms. The remaining mers are those from one or more monomers copolymerizable with the (meth)acrylic acid or ester by free-radical polymerization, preferably vinylaromatic monomers, vinyl esters or vinyl nitriles, and more preferably mers of styrene or acrylonitrile.

In the examples which follow, polymer concentrates (i.e., the segmented copolymer plus any ungrafted components) and polymer blends are tested using standard procedures which are summarized below.

The polypropylene, polymer concentrate, and any additives are blended in the melt on a 7.6 cm by 17.8 cm electric mill with a minimum gap of 3.8 mm set at 190° C. Once the material had fluxed, it is mixed an additional 3 minutes. Higher temperatures are used for higher viscosity materials (for example, mfr=0.5—2 material is done at 195°–210° C.). While still hot, the material is either compression molded or cut into small chunks (about 1–2 cm in each dimension) for granulation (5 mm screen). It is of interest that the additives of the present invention contribute to easy release from hot metal surfaces, such as mill rolls, Haake Rheocord bowls, etc.

The polyolefin blends are compression molded in an electrically heated Carver press 15×15 cm or Farrel press 30.5×30.5 cm. The samples are molded between stainless steel with an appropriate spacer to provide the required thickness 0.25–3.8 mm. In one method the hot melt is taken directly from the mill roll and placed between two stainless steel sheets. This is then placed in the press set at 190° C. and pressed at high pressure (68–91 metric tonnes for the Farrel press and 6820 kg for the Carver press). After three minutes the mold is placed in an unheated press at high pressure for three minutes. In the other procedure, granulated material or pellets produced from an extrusion, Haake, or milling operation are dried and then compression molded. The procedure used is the same as for molding a melt except that a 5 minute preheat is used while maintaining a slight pressure on the press. This is followed by the high pressure molding in the hot and cold presses. A hot press of 190° C. is usually sufficient for mfr=4 polypropylenes, but higher viscosity (lower mfr) polypropylenes would split during sag testing unless higher molding temperatures are used (195°–210° C.).

The sag tests are performed on a compression molded sheet 10×10×0.15 cm. This sheet is clamped in a frame with a 7.6-cm-square opening. There are metal rulers attached to the front and back of the frame for use in measuring sag. The frame and sheet are placed in a hot, forced air oven (typically at 190° C.). The amount of sag of the center of the sheet is then recorded as a function of time. Typically, the sag is first recorded at 2.5 cm but for slow sagging materials sags as low as 16 mm are recorded. Data is recorded up to 10.2 cm of sag or for 30 minutes, whichever occurred first.

The term "slope" refers to the slope of a plot of the natural logarithm of the sag in centimeters versus time, resulting in a straight line. A high slope indicates that the material sags quickly while a low slope indicates that it sags slowly. The advantage of comparing slopes in this manner is that it eliminates any differences in oven cooling when the sample is introduced.

The recoverable compliance test is carried out on a Rheometrics Stress Rheometer. The sample is placed between the parallel plates (1 mm gap) of the rheometer at 190° C. and subjected to a shear stress of 1000 dynes/sq.cm. The stress is applied for 1000 seconds during which time the compliance versus time is recorded. The shear stress is then removed and the sample allowed to recover. The compliance versus time is recorded again and the final compliance at 1000 seconds is determined. The recoverable compliance is the difference between the final compliance of the stress cycle and the final compliance from the recovery cycle. The sample is a small disk (25 mm diameter) cut from a 60 mil (2.12 mm.) plaque, which is prepared by melt blending the sample into the polyolefin on an electric mill at 190° C., then compression molding the plaque in an electrically heated Carver press at 190° C. for three minutes and at 70 metric tonnes with a 60 mil spacer followed by cold pressing for three minutes.

The examples are intended to illustrate the present invention and not to limit it except as it is limited by the claims. All percentages are by weight unless otherwise specified and all reagents are of good commercial quality unless otherwise specified.

EXAMPLES

The following procedure and apparatus is used to prepare the segmented copolymers.

APPARATUS and GENERAL PROCEDURE

A 2 part 1 liter resin kettle with a 4 neck top is equipped with a Teflon paddle stirrer, a thermocouple with a temperature control unit, a heating mantle and a Allihn condenser. (All joints should be ground glass.) The interface between the top and the bottom of the reactor must have a Teflon gasket. The stirrer adaptor apparatus must maintain a vacuum when it is applied to the reaction vessel.

The reactor should be able to maintain the vacuum at the same level at which is supplied, 30 inches of Hg. for at least 15 mm.

Charge polypropylene into the reactor. Degas the reactor and replace with nitrogen 5 times. After the last degassing, allow nitrogen to slowly free flow through the reactor. Mix the styrene-initiator solution and degas with nitrogen for 20 minutes. Pump the solution into the reactor. Commence the swell phase at the recommended temperature. (Preferably, heat the reaction mixture at greater than 1° C./minute directly to 115° C.) When the swell is completed, set temperature controller to 115° C. Reaction will begin. The resulting exothermic event will cause the temperature to reach approximately 140° C. As the temperature drops maintain the temperature at 140° C. Collect the product and dry overnight at 80° C. in a vacuum oven.

Example 1—Blend of 98% Polypropylene and 2% Segmented Copolymer

Step A—Segmented Copolymer

Polypropylene (125 g) beads are added to a 1L kettle type reactor and the system evacuated and refilled with nitrogen. The styrene monomer (30 ml) containing tert-butylperoxy benzoate initiator (200 mg) is degassed by bubbling nitrogen through for 20 m. The monomer-initiator solution is then rapidly pumped into the polypropylene (5 m). While the polypropylene and styrene is stirred the temperature is raised to 90° C. (swell temperature). The temperature is maintained for

1 h (swell time). The temperature is then raised to 140° C. for 2 h. The heating is then removed and the still free flowing pellets are dried overnight at 60° C. in a vacuum oven to yield 146 g of segmented copolymer mixture.

Step B—Blend of 98% Polypropylene and 2% of Segmented Copolymer of Step A

The sag slope of this material is determined as described above and shown to be 0.039 when blended into polypropylene at 2%. The mfr of the blend is 4.18 (condition L of ASTM D-1238.)

(The MFR of the polypropylene is 3 to 5—Condition L.)

The segmented copolymer is extracted continuously with ethyl acetate for 16 h in order to remove the polystyrene homopolymer.

Example 2—Blend

Step A—Segmented Copolymer

The experiment described in example 1 is repeated in order to determine the reproducibility of the swell process. A yield of 145 g of product is obtained.

Step B—Blend of 98% Polypropylene and 2% Copolymer of Step A

A sag slope of 0.046 is measured (2% blended into polypropylene).

Example 3—Blend

Step A—Segmented Copolymer

The experiment in example 1 is repeated but with the following changes. The quantity of polypropylene is increased to 175 g and the initiator level (tert-butyl peroxy benzoate) increased to 500 mg. The temperature is raised to 85° C. at a rate of greater than 2°/minute. A yield of 200 g is obtained. The swell temperature is 85° C. and the swell time is 0.5 h.

Step B—Blend

The blend had a measured sag slope of 0.021 when blended into polypropylene at 1%.

Example 4—Blend

Step A—Segmented Copolymer

The experiment described in example 1 is repeated but with the following changes. The polypropylene quantity is decreased to 85 g and the initiator amount (tert-butyl peroxy benzoate) decreased to 100 mg. The swell temperature is increased to 95° C. and the swell time increased to 2 h. Yield 101 g.

Step B—Blend of 98% PP and 2%

A blend of 98% polypropylene and 2% of the graft copolymer of Step A had a measured sag slope of 0.105 when blended into polypropylene at 2%.

Example 5—Blend

Step A—Segmented copolymer

Polypropylene (100 g), of MFR 4, is placed in a 1L reaction kettle and tert-butylbenzene (400 ml) is added. The reaction vessel and contents are degassed and heated to 160° C. under a nitrogen atmosphere in order to dissolve the polypropylene and subsequently this solution is cooled to 140° C.

The monomer and initiator solution (150 ml of styrene and 357 mg of tert-butyl peroxybenzoate) is deoxygenated by bubbling nitrogen through for 30 min. The monomer and initiator is then pumped into the polypropylene solution at a rate of 2.5 ml per minute while maintaining the temperature at 140° C.

The temperature is held at 140° C. for a further hour and then the reaction allowed to cool to room temperature.

The solvent is removed by heating at 60° C. in a vacuum oven overnight to yield 146 g of segmented copolymer.

Step B—Blend

The segmented copolymer of Step A is milled at 4% into polypropylene (MFR 4) and a plaque prepared. A sag slope of 0.021 is obtained for this plaque.

In one modification of this solution process the monomer styrene above is replaced with a mixture of styrene (142.5 ml) and methacrylic acid (7.5 ml). The plaque prepared from this product (2% into polypropylene of MFR 4) exhibited a sag slope of 0.136. It is believed that this value would extrapolate to a melt strength ratio of less than 5; the reason for poorer, although significant, sag resistance for this variant is not known.

Example 6—Blend 96% PP—4% Copolymer

As in Example 1 but replacing the styrene (30 ml) with styrene (27 ml) and methyl methacrylate (3 ml). This blend has a sag slope of 0.02 when milled into polypropylene at 4%.

Example 7—Blend—96% PP—4% Copolymer

As in Example 1 but increasing the polypropylene quantity to 150 g and replacing the styrene (30 ml) with styrene (32.4 ml) and maleic anhydride (3.3 g) and increasing the initiator quantity (to 240 mg). This blend has a sag slope of 0.0315 when milled into polypropylene at 4%. The blend is exhaustively extracted with ethyl acetate and an infra-red spectrum contained peaks at 18157 cm⁻¹ indicative of the presence of the anhydride in the product and at 700 cm⁻¹ indicative of polymerized styrene.

A blend of this segmented copolymer with a higher Mw polypropylene in a 17.15/82.15 ratio produced a blend with 58% higher Dynatup impact then the unmodified polypropylene.

Example 8—96% Polyethylene 4% Copolymer

As in Example I but replacing the polypropylene (125 g) with polyethylene (150 g) and increasing the styrene (30 ml) to styrene (36 ml) and the initiator (to 240 mg). The blend had a sag slope of 0.036 when blended into polypropylene at 4%.

This segmented copolymer, when added (1515 parts) to a blend of polyethylene and polycarbonate, increases elongation at break by 50%, but tensile modulus is slightly decreased.

Example 9—Blend 96% PP—4% Copolymer

As in Example I but replacing the styrene (30 ml) with styrene (27 ml) and butyl acrylate (3 ml), increasing the polypropylene quantity (to 150 g) and the initiator quantity (to 240 mg). The product had a sag slope of 0.026 when blended into polypropylene at 4% and the exhaustively extracted (with ethyl acetate) blend had peaks at 1730 (polymerized butyl acrylate) cm⁻¹ and 700 cm⁻¹ (polystyrene) in its infra-red spectrum.

Example 10—Blend—96% PP—4% Copolymer

As in Example 1 but replacing the styrene (30 ml) with a mixture of lauryl methacrylate (29 ml) and methyl methacrylate (7 ml), increasing the polypropylene quantity (to 150 g) and the initiator quantity (to 240 mg). The product had a sag slope of 0.086 when milled

into polypropylene at 4% and the exhaustively extracted material (with ethyl acetate) had peaks in its infra red spectrum at 1733 cm⁻¹ and at 700 cm⁻¹.

Example 11—Blend of 96% PP—4% Copolymer

As in Example 1 but replacing the styrene (30 ml) with styrene (21.6 ml), methyl methacrylate (7.2 ml) and N-vinyl-2-pyrrolidone (7.2 ml) and increasing the polypropylene quantity (to 150 g) and the initiator quantity (to 240 mg). The blend had a sag slope of 0.031 when blended into polypropylene (at 4%) and the infra red spectrum of the exhaustively extracted blend (with ethyl acetate) has peaks at 1728 (polymethyl methacrylate) cm⁻¹, 1685 cm⁻¹ (polymerized N-vinyl-2-pyrrolidone) and 700 cm⁻¹ (polystyrene).

Example 12—Blend—96% PP—4% Copolymer

As in Example 1 but replacing the styrene (30 ml) with a mixture of styrene (22 ml) methyl methacrylate (7.0 ml) and glycidyl methacrylate (7.0 ml) and increasing the polypropylene quantity (to 105 g) and the initiator quantity (to 240 mg). The blend had a sag slope of 0.036 when blended into polypropylene at 4%. The exhaustively extracted blend (with ethyl acetate) exhibited peaks in the infra-red at 1729 cm⁻¹ (polymerized methacrylates) and 700 cm⁻¹ (polystyrene).

Example 13—Blend—96% PP—4% Copolymer

As in Example 1 but replacing the styrene (30 ml) with a mixture of styrene (21.6 ml) methyl methacrylate (10.8 ml) and maleic anhydride (3.3 g) and increasing the polypropylene and initiator amounts (to 150 g and to 240 mg respectively). A blend of 96% polypropylene and 4% of the copolymer (styrene, methyl methacrylate and maleic anhydride) has a sag slope of 0.042. The exhaustively extracted blend (ethyl acetate) exhibited peaks in the infra red at 1720 cm⁻¹ (methyl methacrylate) at 1780 cm⁻¹ and 1856 cm⁻¹ (polymerized maleic anhydride) and at 700 cm⁻¹ (polymerized styrene).

Example 14

A 1L pressure reactor is charged with polypropylene mfr=4, (believed prepared by the process of European Patent Application 437,808) (50 g), styrene (50 g), initiator (tert-butyl peroxy benzoate, 200 mg) and deionized water (343 g). The system is heated to 140° C. under a nitrogen atmosphere and at a pressure of 44 psi. It is held at this temperature for 1 h. Only a small amount of agglomeration of the polymer is observed in the reactor. The reaction is cooled and the copolymer collected by filtration and then dried in a vacuum oven to yield 97.7 g of material. A blend of this material with 4% polypropylene had a sag slope measured at 0.03.

Example 15

A blend is prepared of 5 weight percent of the segmented copolymer of Example 3 in Himont 6523, homopolymer of propylene, mfr 3.5–4.5 grams/10 minutes, ASTM 1238. The flow rate of the neat segmented copolymer is 0.02 grams/10 minutes at the same test temperature. The crystallization temperature of the neat segment copolymer is 116.6° C.

Other properties are compared below.

Test	Control PP	5% Blend
Tensile Modulus (ASTM D638)	216,900 psi (1494 mPa)	244,100 psi (1681 mPa)

-continued

Test	Control PP	5% Blend
Notched Izod Impact (ASTM D256)	0.47 ft.lb/in (25 J/m)	0.64 ft.lb/in (34 J/m)
Load at Break (ASTM D638)	45.3 lbs. (20.6 kg)	52.0 lbs (23.6 kg)
Stress at Break (ASTM D638)	3340 psi (2.3 mPa)	3607 psi (2.49 mPa)
DSC Crystallization Temp.	109.6° C.	122.6 (2% blend)

This increased modulus, impact, load at break and stress at break are attractive properties for a blend useful in commercial thermoforming and packaging application, as is the enhanced nucleation seen.

Example 16

The conditions of Example 3 are repeated, except that there is no hold time at 85° C. The sag slope of this segmented copolymer at the 2% level in the referenced polypropylene is negligible (below 0.02).

Example 17

A blend is made of 5 weight percent of the segmented copolymer of Example 16 with Aristech Ti 4007F, believed to be a copolymer of propylene with 7.4% ethylene, mfr 0.7. The polymer is chosen because it has good impact strength at room and refrigerator temperatures and contains additives which qualify it for food packaging uses. Properties are shown below: the higher extrusion rate (for a 0.10 inch (2.5 mm.) sheet appears to be a consequence of the improved melt strength which permits faster extrusion without breaking. The wider thermoforming window allows commercial production of parts without "webbing" (holes or tears formed by exceeding the thermoformability of the polymer at a set temperature) over a wider temperature range. To determine the thermoforming window, the values are normalized to the behavior of an unmodified polyolefin sheet, and what is determined in a standardized thermoforming operation is the relative temperature range over which an acceptable part can be formed. A sheet of polypropylene, modified or unmodified, is produced by a 2.5 inch (63.5 mm) extruder, and cut to a 0.100"×21.5"×27" sheet (2.54 mm.×0.546 m×0.686 m). The sheets are then formed in a 4-cavity mold in a Brown thermoformer. The mold has depressions of various sizes, which allows the modified polyolefin to be tested for thermoformability under a variety of stretch and orientation conditions, simulating practical thermoforming of commercial articles. The thermoforming window is the temperature range over which a good part can be formed. A good part is one that does not contain any warpage or "folding over" in the part. These windows are reported as "normalized values" relative to the window of the unmodified material.

Test	Control PP	5% Blend
Vicat Softening Temp. (ASTM D-1525)	142.9° C.	145.4° C.
DTUFL (ASTM D-648)	48.7° C., 264 psi (1.81 mPa)	52.7° C., 264 psi (1.81 mPa)
Melt Flow rate (ASTM 1238)	0.74 g/10 min.	0.56 g/10 min.
Extrusion Rate	72.6 lb/hr (33 kg/hr)	85.7 lb/hr (38.9 kg/hr) 82.5 lb/hr (37.5 kg/hr) (at 3% additive)
Relative Thermo-	1	2.08

-continued

Test	Control PP	5% Blend
forming Window		1.44 (at 3% additive)
Recoverable Compliance	8.9×10^{-5} cm ² /dyne	19.5×10^{-5} cm ² /dyne

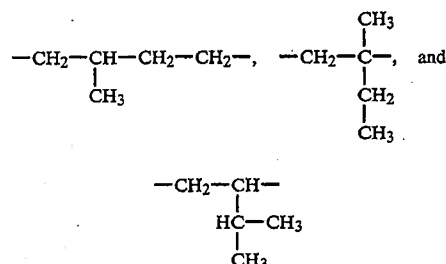
The recoverable compliance appears to relate directly to the ability to resist sag; a higher value for the compliance of the blend correlates with a lower sag value and with better thermoforming properties.

Example 18

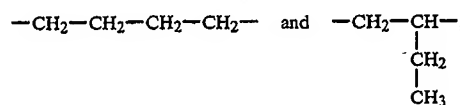
The preparation of Example 16 is repeated but with substitution of 1,1-bis(tert-butylperoxy)3,3,5-trimethylcyclohexane, half-life 18.6 minutes at 125° C. In this example, the temperature is raised directly to 125° C. at a rate exceeding 2° C./minute. The resulting segment copolymer exhibits good resistance to sag at the 2% level in polypropylene.

Example 19

In this example are reported data on sag resistance of polypropylene when modified by block copolymers of styrene and a hydrogenated conjugated diene polymer block. Such hydrogenated diene polymer blocks are "polyolefins", but are not prepared by the polymerization of a mono-olefin. Thus a block from hydrogenated polyisoprene has the units



and a block from hydrogenated polybutadiene has the units



resembling a copolymer of ethylene and butene-1.

The materials used in this comparison are:

- Polypropylene homopolymer, MFR-4, no additive
- PP, 4% 30% styrene/70% butadiene block copolymer, 80% diblock, 20% triblock

PP, 4% diblock copolymer, 37% styrene, 63% hydrogenated polyisoprene

PP, 4% triblock copolymer, 29% styrene, 71% hydrogenated butadiene

PP//methyl methacrylate segmented copolymer, Example 69 of U.S. Pat. No. 4,957,974.

The graft copolymer of the present invention is not evaluated in this series. However, it is fully anticipated by much cross-comparative work with Example 29-E that a sag slope value of less than 0.02 would be obtained.

The blends are mixed on a two-roll mill at 195° C. First the polypropylene is placed on the mill and pro-

cessed to a smooth rolling bank. Then the modifier candidate is added to the mill and the material is blended for five minutes. The material is transferred to a preheated mold (0.15×24×24 cm plaque) and pressed at 195° C. for three minutes. The mold is then transferred to a cold press and cooled under pressure. A 10 cm×10 cm square is cut from the plaque and clamped into the sag frame. The sample is then transferred to a 190 degree oven with a glass window for observation of sag. The amount of sag as a function of time is measured.

Test	Formulation				
	A	B	C	D	E
Time to Sag 1 inch (25.4 mm)	8:32	7:11	—	8:21	26:49
Time to Sag 2 inch (50.8 mm)	10:50	9:30	8:52	10:50	—*
Sag slope	0.30	0.30	0.29	0.26	0.022

*Value for 2 minutes beyond length of time of experiment

The following examples illustrate preparation of the segmented copolymer by the process of the invention. In all cases, the polypropylene homopolymer used in the synthesis had a melt flow rate ca. 4; where noted, the polypropylene as supplied had a porous structure. The polypropylene used in the sag test also had a mfr of 4.

Preparations of PP-PS with Different Initiators

Example 20

With tert-butyl peroxybenzoate:

The initiator tert-butyl peroxybenzoate (0.5 g, 2.57 mmoles) is added to the polypropylene (175 g, 4.13 moles, porous) in a 500 ml round bottomed flask followed by the styrene monomer (18.4 g, 0.177 moles). The flask is then placed on a rotary evaporator and the system purged with nitrogen for 5 minutes. The purging is followed by rotation of the flask on the rotary evaporator for 1 minute and then another 5 minute purge with nitrogen.

Then while the flask is rotating on the rotary evaporator the temperature of the reaction mixture is raised to 140° C. at a rate of 2.1° C./min by means of an oil bath under the 500 ml flask. The temperature is maintained at 140° C. for 2 hours and then the still free flowing beads dried overnight at 70° C. under vacuum to yield 192 g of product.

The product is blended into polypropylene at 4% and a 60 mil (1.52 mm) plaque prepared as described previously. A piece from the plaque is tested by the sag test and found to sag only $\frac{1}{4}$ " in 30 minutes, i.e., its sag slope value would be < 0.02.

Example 21

With dicumyl peroxide:

A) The styrene monomer (18.4 g, 0.18 moles) and dicumyl peroxide initiator (0.69 g, 2.57 mmoles) are premixed and then added to the polypropylene (175 g, 4.13 moles, porous) in a 500 ml round bottomed flask. The round bottomed flask is placed on a rotary evaporator. The entire system is purged with nitrogen for 5 minutes followed by a rotation for 1 minute and a further 5 min purge with nitrogen.

The temperature of the reaction mixture is raised to 151° C. at a rate of 1.5° C./min by means of an oil bath. The temperature is held at 151° C. for a further 2 hours and then the product dried overnight at 60° C. under

vacuum to yield 193.2 g of product. The sag slope of the product is 0.21 when milled into polypropylene at 4%.

B) The styrene monomer (19.4 g, 0.19 moles) and the dicumyl peroxide initiator (0.45 g, 1.65 mmoles) are premixed and deoxygenated by bubbling nitrogen through for 15 minutes. The monomer-initiator mixture is then pumped onto the polypropylene (175 g, 4.13 moles, porous) which is under an inert atmosphere in a 500 ml resin kettle.

The reaction temperature is raised to 150° C. by means of a heating mantle at a rate of 2.2° C./min. The reaction mixture is held at this temperature for 2 hours and then is dried at 60° C. overnight to yield 192.4 g of free flowing product whose sag slope is measured at 0.16 when blended at 4% into polypropylene.

Example 22

With tert-butyl peroxyisobutyrate:

Styrene monomer (27.3 g, 0.26 moles) and tert-butyl peroxyisobutyrate (0.51 g, 2.37 mmoles) initiator are premixed and deoxygenated by bubbling nitrogen through for 10 minutes. The monomer and initiator solution is then pumped into the polypropylene (175 g, 4.13 moles, porous) which is under a nitrogen atmosphere in a 500 ml resin kettle.

The reaction temperature is raised to 116° C. at a rate of 1° C./min by means of a heating mantle and held at this temperature for 2 hours. The final material, 199.9 g of still free flowing beads is isolated following drying at 60° C. overnight.

The product is milled at 4% into polypropylene and a plaque prepared in the usual manner. The measured sag slope is 0.21.

Example 23

With tert-butyl peroxoate:

In this experiment the styrene monomer (27.3 g, 0.26 moles) and the initiator tert-butyl peroxoate (0.56 g, 2.57 mmoles) are premixed and deoxygenated as before and then pumped onto the polypropylene (175 g, 4.13 moles, porous) which is in a 500 ml resin kettle. The temperature is raised to 106° C. at a rate of 0.8° C./min by means of a heating mantle and held there for 2 hours. The product is dried overnight at 60° C. to yield 199 g of material. The product is tested as above and its sag slope is 0.20.

Example 24

With benzoyl peroxide

The reaction is carried out in the same manner as with tert-butyl peroxybenzoate except that the monomer and initiator are premixed before addition to the polypropylene since in this case the initiator is a solid. Thus in this reaction the styrene monomer (27.3 g, 0.26 moles) and benzoyl peroxide initiator (0.62 g, 2.57 mmoles) are premixed and added to the polypropylene (175 g, 4.13 moles, porous) and the reaction carried out in a 500 ml round bottomed flask on a rotary evaporator. The temperature is raised to 104° C. at a rate of 2.7° C./min by means of an oil bath and held at this temperature for 2 hours before isolating 199.7 g of product after drying overnight. Sag slope is 0.21 at 4% into polypropylene.

Example 25

With Di-tert-Butyl Peroxide:

Styrene monomer (17.50 g, 0.168 moles) and di-tert-butyl peroxide (0.24 g, 1.65 mmoles) are, mixed to-

gether, stirred and deoxygenated by bubbling nitrogen through for 5 minutes. Then the initiator-monomer mixture is pumped rapidly (over 5 minutes) onto the polypropylene (175 g, 4.13 moles) which is in a 500 ml resin kettle under nitrogen.

The reaction mixture is stirred while the temperature is raised to 155° C. at a rate of 2.7° C./Min by means of a heating mantle. This reaction is maintained at 155° C. for a further 2 hours and then the material dried overnight at 60° C. under vacuum to yield 188.2 g of product. This product is milled into polypropylene at 4% and the sag slope of the resulting plaque is 0.09.

Example 26

With 1,1-di-(tert-butyl-peroxy)-3,3,5-trimethylcyclohexane:

A) Styrene monomer (18.4 g, 0.18 moles) and initiator (0.39 g, 1.28 mmoles) are mixed together and added to a 500 ml round bottomed flask containing the polypropylene (175 g, 4.13 moles). The round bottomed flask is placed on a rotary evaporator and evacuated to a vacuum of 20 inches (ca. 500 mm) of Hg. The vacuum is released into nitrogen. The evacuation and releasing is repeated three times and the reaction mixture is heated to 127° C. at a rate of 1.7° C./mm. The temperature is then maintained at 127° C. for a further 2 hours and then the material is dried overnight at 60° C. to yield 192.9 g of product.

The sag slope of this material is 0.028 when blended into polypropylene at 4%.

B) Styrene monomer (27.27g, 0.26 moles) and initiator (0.39 g, 1.28 mmoles) are premixed and added to the polypropylene (175 g, 4.13 moles) followed by evacuation and inertion as before. The temperature is raised to 140° C. at a rate of 2.6° C./min and maintained at this temperature for 40 min. The material is dried at 60° C. overnight to yield 200 g of product.

The sag slope of this material is 0.023 when blended into polypropylene at 4%.

Example 27

In the following table are compared the sag values of various segmented copolymers and the one-hour half-life of the initiators used.

Initiator	Example	One-hour half-life, °C.	Sag Resistance?
Benzoyl peroxide	24	92	No
tert-Butyl peroxyoctoate	23	95	No
tert-Butyl peroxyisobutyrate	22	102	No
1,1-Di-(tert-butyl-peroxy)-3,3,5-trimethylcyclohexane	26	115	Yes
tert-Butyl peroxybenzoate	20	125	Yes
Dicumyl peroxide	21	137-9	No
Di-tert-butyl peroxide	25	149	Moderate*
Control (PP homopolymer)			No**

*Melt strength ratio = 2.3

**Sag value = 0.21

Example 28

Blends of Polypropylene and Polystyrene.

Blends of polypropylene (mfr=4) and polystyrene (Dow Styron 685D, M_w 330,000) are prepared on the mill roll and plaques pressed afterwards in the usual

manner. The blends are produced in the absence and in the presence of a PP-PS copolymer which is prepared with the aid of the initiator benzoyl peroxide (Example 24).

Blend Components		
Blend		Sag Slope
1.	50 g Polypropylene + 50 g polystyrene	0.09
2.	50 g Polypropylene + 50 g polystyrene + 4 g (Example 26)	0.07
3.	80 g Polypropylene + 20 g polystyrene	0.23
4.	80 g Polypropylene + 20 g polystyrene + 4 g (Example 26)	0.16
5.	100 g Polystyrene	<0.02

This example shows that certain segmented copolymers of the present invention which do not show good sag resistance in polypropylene can produce improved sag resistance (over a similar blend with no compatibilizer) when used to compatibilize fairly large amounts of polystyrene with polypropylene.

Example 29

Production of Segmented Copolymer in a Reactor with Baffles

Polypropylene (23.5 Kg, mfr=4) is added to a 2.2 Cu. Ft. (62.3 l.) Porcupine Processor (The Bethlehem Corporation, Easton, Pa., USA), which is a reactor equipped with stirring paddles and many small baffles, followed by styrene monomer (2.45 Kg) and then t-butyl peroxybenzoate initiator (67.1 g).

The reactor is sealed and then inerted by evacuating to 30 inches Hg (760 mm.) and then filling with nitrogen to atmospheric pressure. The evacuation and release into nitrogen is done three times in succession.

The reactor contents are heated at atmospheric pressure at a rate of 3° C./Min to a final temperature of 140° C. The reactor is equipped with a water cooled condenser. Heating is accomplished by means of high pressure steam passing through the stirring paddles. This reaction temperature is maintained for 2 hours. After this time, the steam heating is removed and the reactor pressure is reduced from atmospheric to 30 inches Hg (760 mm.). The reactor contents are dried in this manner for 2.5 hours and then the product (25.5 Kg) collected.

The sag slope of this material in a blend with polypropylene is measured in the usual manner and the plaque sags to less than $\frac{1}{2}$ " (12.7 mm.) in 25 minutes. This value correlates to a melt strength ratio of at least 5.

Examples 30 and 31

These examples illustrate the importance of the heat-up rate and should be compared with Examples 20 and 26. Although segmented copolymer of polypropylene and polystyrene is formed, the resulting polymers, when prepared at a low heat-up rate, are much less effective in controlling sag when blended with polypropylene.

For Example 30, the polypropylene (175g, 4.1 moles) is added to a 500 ml round bottomed flask and inerted with nitrogen. The styrene monomer (18.4 g, 0.17 moles) and t-butyl peroxybenzoate initiator (0.5 g, 2.57 mmoles) are combined and deoxygenated by bubbling nitrogen through for about 15 minutes. Then the monomer and initiator solution are pumped onto the polypropylene under nitrogen. The temperature of the reaction

mixture is raised to 142° C. at a rate of 0.5° C./Min. The temperature is held at close to 140° C. for 2 hours and then dried. The sag slope of the product is measured at 4% in polypropylene and shown to be 0.14 (melt strength ratio=1.5). In a similar manner (Example 31), a product is prepared from polypropylene (175 g), styrene (18.4 g), and the initiator 1,1 bis (tert-butylperoxy)-3,3,5-trimethylcyclohexane (0.388 g, 1.28 mmoles). However with this initiator, the temperature is raised to 127° C. at a rate of 0.6° C./Min. The sag slope of this product is measured at 4% in polypropylene and shown to be 0.21 (melt strength ratio=1.0).

Example 32

A blend of polypropylene (mfr=4) and polystyrene (similar to that used in Example 28) is prepared at a 7:3 ratio. Addition of 5.5 weight-percent of a segmented copolymer similar to that of Example 29 doubles the elongation at break, with slight improvement in impact strength and tensile modulus, but with some lowering of tensile stress at break.

Example 33

To a blend of 20 parts poly(phenylene oxide) and 80 parts polypropylene (mfr=4) is added 5.5 or 9 parts of the segmented copolymer similar to that of Example 29. A slight increase in tensile modulus is seen. Blends where the ratio of the matrix polymer is 50:50 or 40:60 may also be prepared with the segmented copolymer.

Example 34

In a manner similar to Example 33, blends of polycarbonate/polypropylene (70/30 or 80/20) may be modified with up to 10 parts of the segmented copolymer of Example 29.

What is claimed is:

1. A process for preparing a segmented copolymer of polypropylene or polyethylene with polystyrene which segmented copolymer is essentially free of ungrafted polystyrene and which imparts improved melt strength to polypropylene which comprises:

(a) mixing the polypropylene or polyethylene with styrene (and optionally up to about 20% by weight, based on total monomer content, of one or more monomers copolymerizable with styrene) in the presence of an initiator having a one-hour half-life at a temperature in the range of from about 110° C. to about 125° C.;

(b) heating the mixture at a rate of at least 1° C./minute to a temperature of at least 90° C. at which the polypropylene or polyethylene completely swells; and

(c) continuing heating at a rate of at least 1° C./minute to at least 140° C. until grafting occurs.

2. The process of claim 1 wherein the mixture contains polypropylene, and wherein the mixture is heated directly to a temperature of at least 140° C.

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EXHIBIT E

(12) **United States Patent**
Cahill et al.

(10) **Patent No.:** **US 6,346,308 B1**
 (45) **Date of Patent:** ***Feb. 12, 2002**

(54) **ACTIVE OXYGEN SCAVENGER
 COMPOSITIONS AND THEIR USE IN
 PACKAGING ARTICLES**

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(73) **Assignee:** **BP Corporation North America Inc.**, Chicago, IL (US)

(*) **Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) **Appl. No.:** **09/485,517**

(22) **PCT Filed:** **Mar. 17, 1998**

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§ 102(e) Date: **May 9, 2000**

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PCT Pub. Date: **Apr. 1, 1999**

Related U.S. Application Data

(63) Continuation-in-part of application No. PCT/US98/02991, filed on Feb. 17, 1998, and a continuation-in-part of application No. PCT/US97/16712, filed on Sep. 22, 1997, and a

continuation-in-part of application No. 08/717,370, filed on Sep. 23, 1996, now Pat. No. 6,083,585.

(51) **Int. Cl.⁷** **B29D 22/00**

(52) **U.S. Cl.** **428/35.7; 428/474.4; 525/168; 525/171; 525/177; 525/445; 528/298; 252/186.1**

(58) **Field of Search** **428/474.4, 35.7; 525/168, 171, 177, 445; 528/298; 252/186.1**

(56) **References Cited**

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* cited by examiner

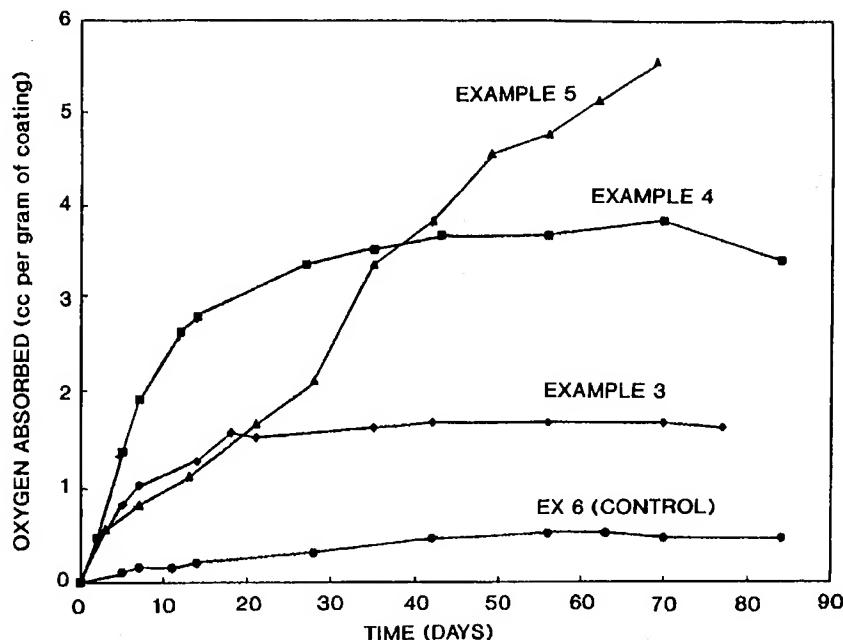
Primary Examiner—Leszek Kiliman

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(57) **ABSTRACT**

Active oxygen scavenging compositions and their use in packaging articles are disclosed. The compositions are all plastic materials and are typically deployed as at least one layer in a multi-layered wall of a packaging article such as a bottle, can or film. The compositions are usually used in conjunction with added transition metal catalyst to enhance the uptake of oxygen. Use of the compositions and package constructions disclosed serves to lengthen the shelf life of packaged oxygen sensitive substances and/or diminish the need for refrigeration of the packages.

25 Claims, 4 Drawing Sheets



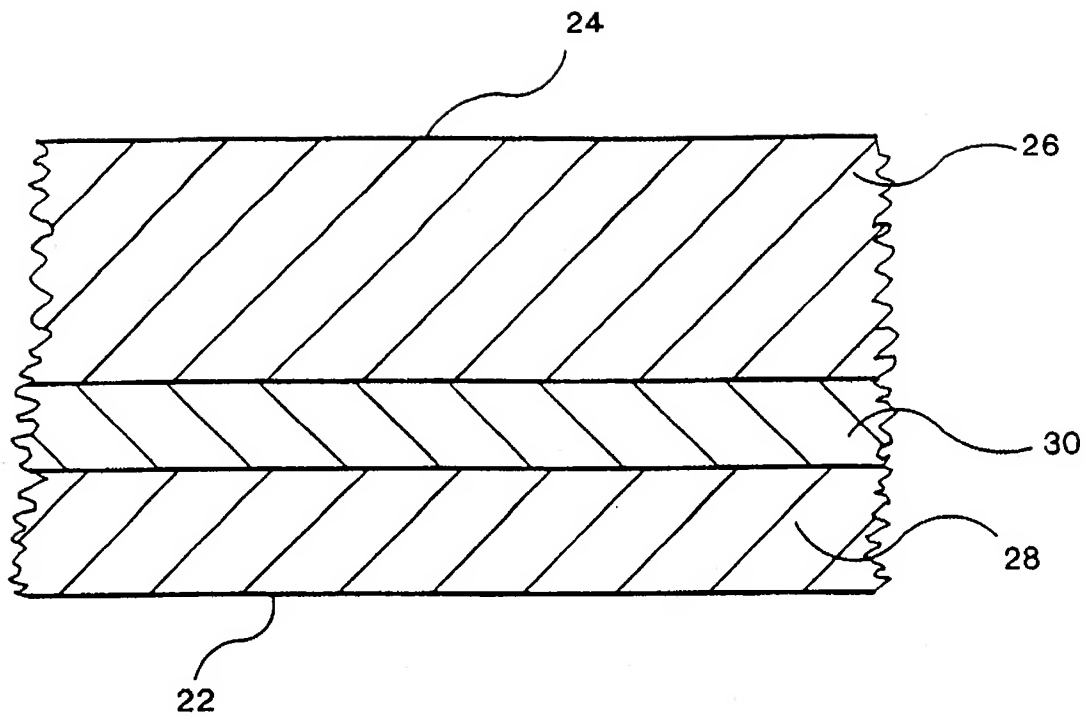


FIG. 1

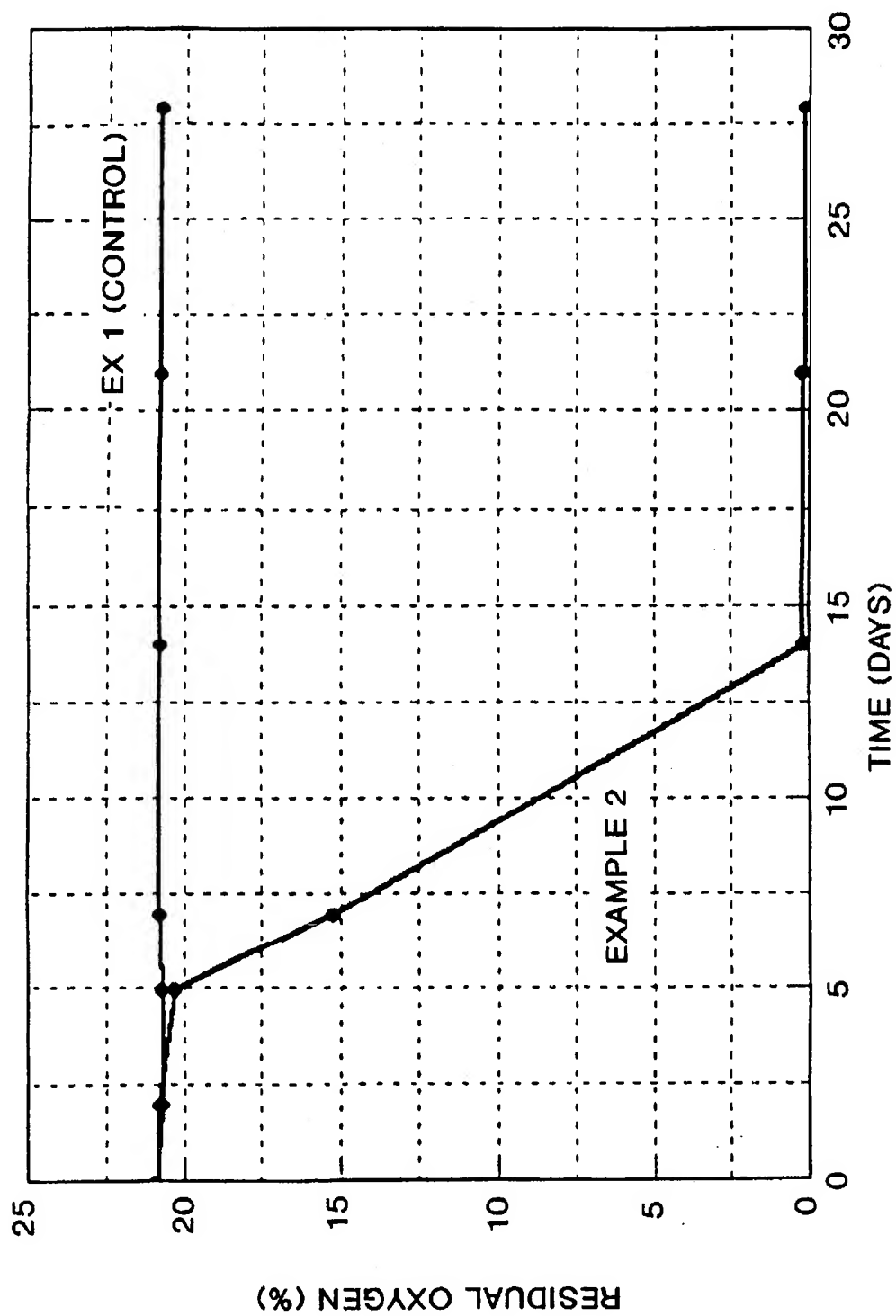


FIG. 2

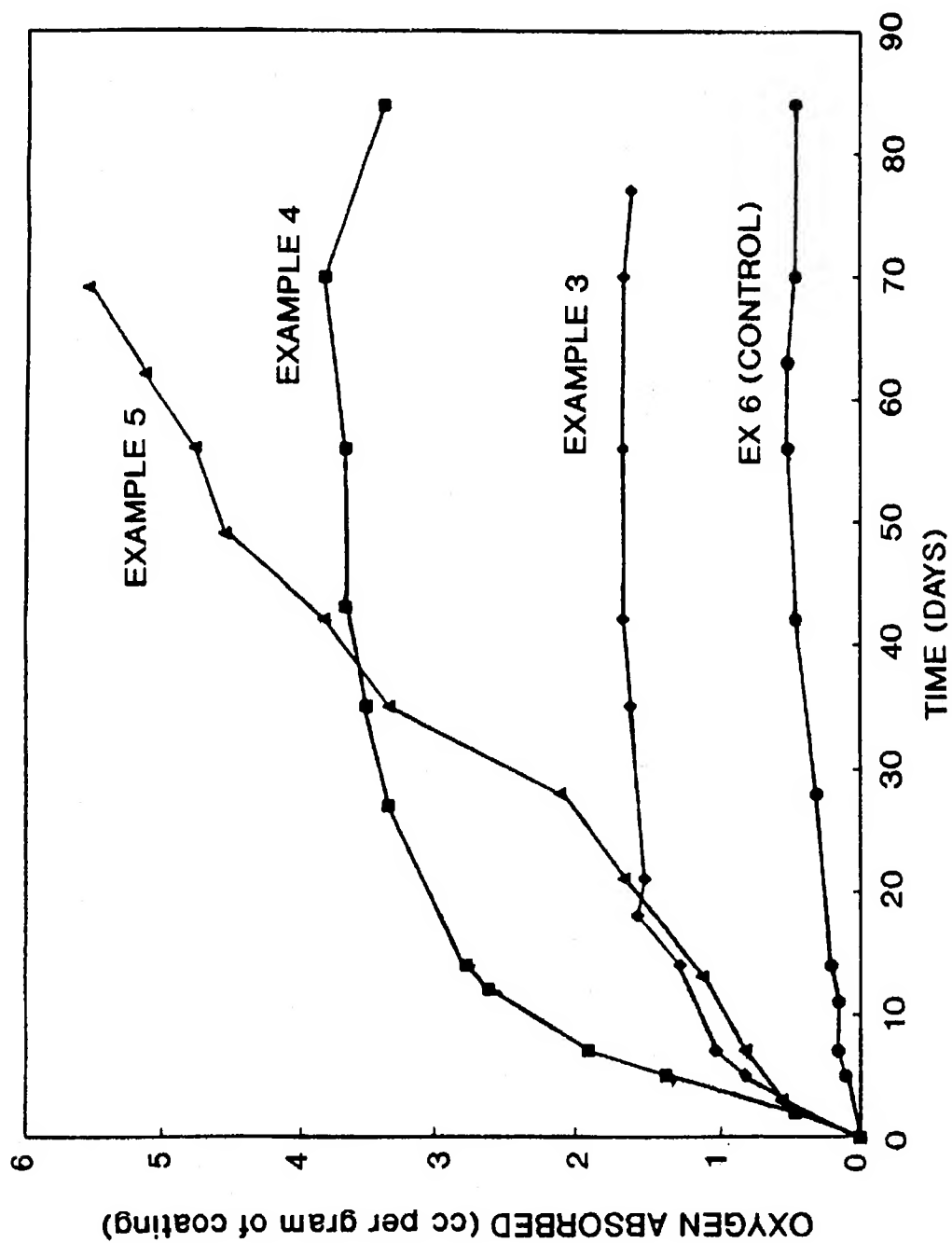


FIG. 3

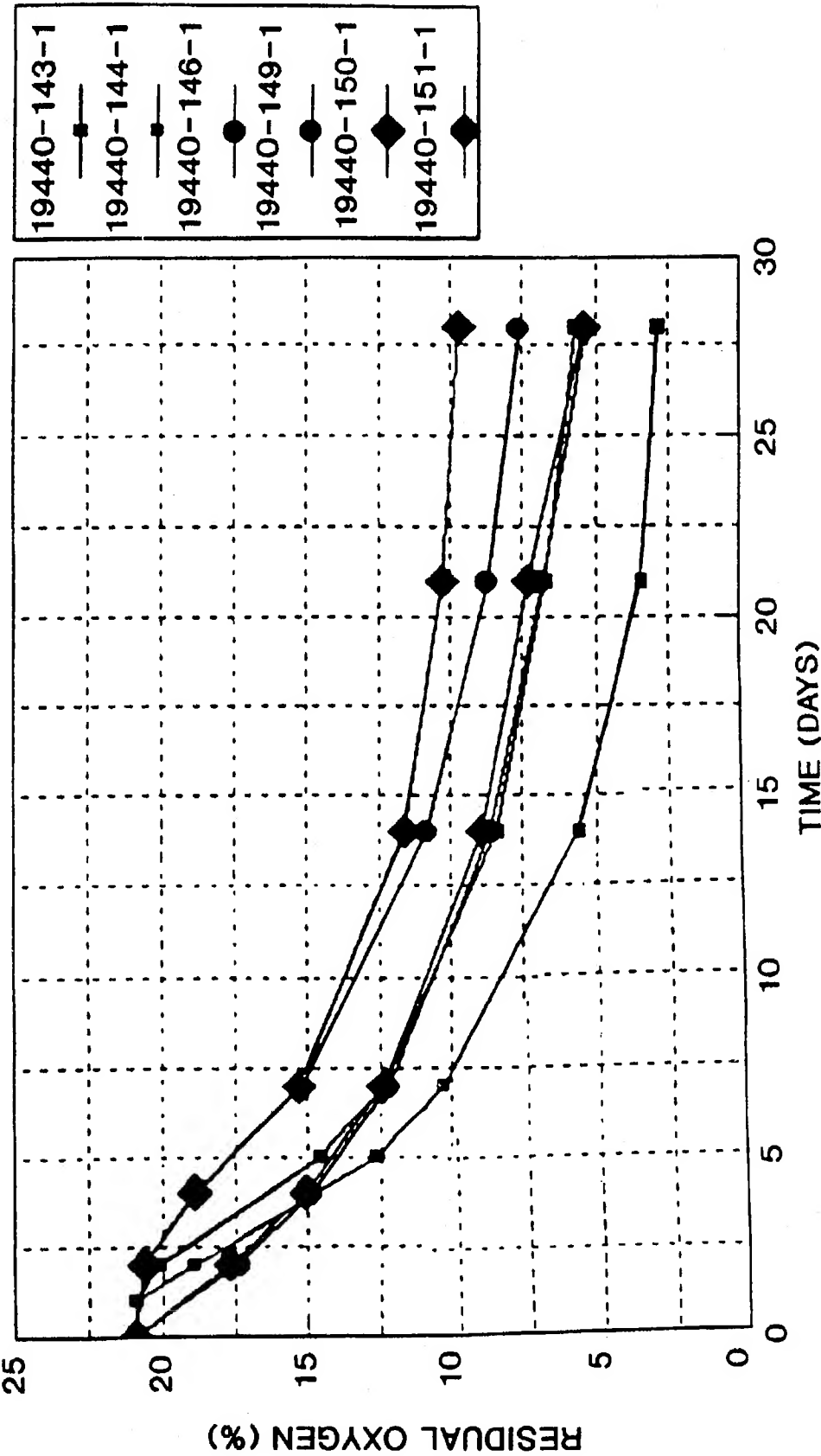


FIG. 4

ACTIVE OXYGEN SCAVENGER COMPOSITIONS AND THEIR USE IN PACKAGING ARTICLES

RELATIONSHIP TO PRIOR APPLICATIONS

This application is a continuation in part of a US application filed on Sep. 23, 1996 having Ser. No. 08/717,370 now U.S. Pat. No. 6,083,585. It is also a continuation in part of a PCT application filed on Sep. 22, 1997 having Application Number PCT/US97/16712 and a continuation in part of a PCT application filed on Feb. 17, 1998 having Application Number PCT/US98/02991.

STATEMENT REGARDING FEDERALLY FUNDED RESEARCH

(Not Applicable)

FIELD OF THE INVENTION

The invention generally relates to compositions having active oxygen scavenging capacity and the use of these compositions for improved packaging of oxygen sensitive substances. Formulations are disclosed which may be fabricated into packaging articles or used as container liners/coatings.

BACKGROUND OF THE INVENTION

Plastic materials have continued to make significant advancements into the packaging industry due to the design flexibility of their material and their ability to be fabricated in various sizes and shapes commonly used in the packaging industry. The deployment of plastic materials into packaging articles such as films, trays, bottles, cups, bowls, coatings and liners is already commonplace in the packaging industry. Although plastic materials offer the packaging industry many benefits with an unlimited degree of design flexibility, the utility of plastic materials has remained inhibited in situations where barrier properties to atmospheric gases (primarily oxygen) are necessary to assure adequate product shelf life. When compared to traditional packaging materials such as glass, steel or aluminum, plastics offer inferior barrier properties which limits their acceptability for use in packaging items that are sensitive to atmospheric gases, particularly when the exposure to the atmospheric gases will entail extended time periods. The packaging industry continues to seek packaging materials which offer the design flexibility of plastics and at the same time have the barrier properties of glass, steel or aluminum.

It should be recognized that there are two broad types of barriers for shielding packaged oxygen sensitive substances from oxygen (generally oxygen from air). One is known as a passive oxygen barrier and finds utility because of superior resistance to the permeation of oxygen through such constructions. Glass and metal are essentially perfect passive oxygen barriers. Condensation polymers, particular polyesters such as polyethylene terephthalate (PET) have found wide acceptance in the packaging industry and are moderately good passive oxygen barriers. Polyamides, such as polyhexamethylenedipamide and polyphthalamides, are generally better passive oxygen barriers than polyesters when deployed in similar constructions.

The other type of oxygen barrier is known as an active oxygen barrier. An active oxygen barrier is a substance capable of intercepting and scavenging oxygen (by undergoing chemical reaction with the oxygen), for example, as the oxygen attempts to permeate through the packaging. A

major salient feature of active oxygen scavengers is their ability not only to intercept oxygen from air as it attempts to reach the package cavity but also to provide the means to eliminate unwanted oxygen (often called head space oxygen) from within the package cavity wherein said oxygen may have been inadvertently introduced during packaging or filling. Only active oxygen scavengers can remove unwanted oxygen from the package cavity. Active oxygen scavenging implies, therefore, consumption of a material incorporated in the package. The material is progressively consumed so that the active oxygen scavenging ability is eventually depleted or at least diminished. However, this eventual depletion of the active oxygen scavenging moiety can be adjusted so that the depletion occurs only well after the required oxygen free shelf life of the packaged product which is typically one year or less.

Active oxygen scavengers are known and have been used in a variety of constructions. Optimally, active oxygen scavengers should have as many as possible, or at least some, of the features recited below:

- (1) Their oxygen scavenging ability should be present both in the absence and/or in the presence of water or moisture.
- (2) They should have clarity similar to that of PET or other packaging thermoplastics when necessary for production of clear bottles or films.
- (3) They should be self-adherent to adjacent layer(s) when used as layer(s) in a multi-layer package construction.
- (4) They should be evenly dispersed throughout the package so as to afford optimum and uniform opportunity to scavenge oxygen.
- (5) They should have glass transition temperatures above filling and storage temperatures (at least above about 30° C.) so that they exist as solids or solid films for these purposes.
- (6) When used as a container liner, they should be capable of being sprayed onto the inner surface of a container from an aqueous system (as opposed to a lacquer which would require evaporation of organic solvents).
- (7) The decomposition products to which the active oxygen scavengers are decomposed after reaction with oxygen must not be deleterious to the packaged product or must be shielded from the packaged product.
- (8) The mechanism of their reaction with oxygen must not be deleterious to the strength, clarity, or other salient features of the packaging article.

What is needed are active oxygen barrier materials possessing as many as possible of the features recited above, which may be produced at reasonable cost, and which have sufficient oxygen scavenging and barrier properties to offer the possibility of target shelf lives in the range of six months to two years for oxygen sensitive products. This invention further addresses such need.

INVENTION SUMMARY AND REVIEW OF PRIOR ART

In a commonly assigned, related, and co-pending US application filed on Sep. 23, 1996 and having Ser. No. 08/717,370, now U.S. Pat. No. 6,083,585 it was disclosed that certain hydrocarbons, such as polyolefins, (especially polydienes) when present in small amounts as polyolefin oligomer blocks in a block copolyester polymer added substantial active oxygen scavenging capacity to packaging polyesters which showed no active oxygen scavenging capacity what-so-ever in the absence of the polyolefin

oligomer blocks. The oxygen scavenging copolyesters of the above-referenced application were comprised predominantly of packaging polyester segments with only an oxygen scavenging amount of polyolefin oligomer segments present to supply the oxygen scavenging capacity required for the intended packaging application. The copolyesters of the application having Ser. No. 08/717,370 now U.S. Pat. No. 6,083,585 were typically in the range of about 0.5–12 wt % polyolefin oligomer segments with the remainder comprising polyester segments. An especially preferred embodiment was a copolyester of about 4 wt % polyolefin oligomer segments with the remainder being polyester segments. Such block copolyesters comprising low weight percent levels of polyolefin oligomer segments have properties (such as melting point, viscosity, and clarity) very similar to the unmodified polyester from which the polyester segments were derived. In particular, layers in laminar packages and bottles having one or several layers of unmodified polyester and one or several layers of oxygen scavenging block copolyester as described above, were self-adherent and packaging articles appeared to be a monolithic (rather than layered) construction.

In related PCT Application Number PCT/US98/02991 which was filed on Feb. 17, 1998 the concept of implanting high capacity oxygen scavenging polyolefin oligomer segments was extended to polyamides. The above referenced PCT application disclosed block copolyamides comprising predominantly polyamide segments and an oxygen scavenging amount of polyolefin oligomer segments. As was the case for the earlier disclosed copolyesters, the corresponding copolyamides had properties very similar to unmodified polyamides, especially the polyamide from which the polyamide segments were derived. Polyamides are generally considered to be an inherently superior passive barrier as compared to polyesters. Thus copolyamides not only had substantial active oxygen scavenging capacity but also had improved passive barrier properties since they were comprised mainly of polyamide segments. In this application, additional oxygen scavenging moieties are disclosed which when incorporated into copolyesters or copolyamides exhibit the superior active oxygen scavenging capacity as was demonstrated in related prior applications. Also disclosed is the incorporation of active oxygen scavenging moieties into other polycondensates in addition to copolyamides and copolyesters. Further disclosed is the incorporation of active oxygen scavenging moieties into addition type (as opposed to condensation type) copolymers. Another embodiment of this application involves the incorporation of the previously disclosed oxygen scavenging moieties (such as polybutadiene oligomer) into an aqueous based spray formulation for use as a container liner/coating for removal of head space oxygen from canned goods via active oxygen scavenging.

In earlier and related patent applications previously cited above, it was disclosed that certain hydrocarbon materials could be adapted for deployment as active oxygen scavengers in packaging articles. These active oxygen scavengers when placed in the walls of a packaging article would intercept and react with oxygen (from air) as it attempted to pass through the package wall thereby shielding the package contents from oxygen and extending the useful shelf life of the packaged oxygen sensitive substance. When used in packaging, active oxygen scavengers can also react with and remove head space oxygen from the package cavity provided that means exist for oxygen in the package cavity to contact and react with the active oxygen scavenger. The ability of hydrocarbons to react with oxygen is well known

in the art and began to attract research attention in the early twentieth century because of the unwanted degradation of such materials as automobile tires and vegetable oils. Eventually, it was recognized that the propensity of hydrocarbons to oxidize could be used to advantage in packaging when deployed as active oxygen scavengers. However, it was necessary to overcome two major obstacles in order to reduce the phenomenon to practice. First, it was necessary to identify those hydrocarbons which were reasonable to use from an economic view but which also had sufficient oxygen scavenging capacity to provide the desired shelf life. Secondly, it was necessary to find a way to innocuously incorporate these materials into modern packaging articles which could be fabricated using current state-of-the-art packaging equipment. Other considerations included clarity of the package and fitness for recycle of the package. These issues were addressed and largely resolved in earlier and related patent applications previously cited above.

In those earlier and related applications, it was disclosed that hydrocarbons such as polyolefin oligomers had sufficient commercial oxygen scavenging capacity to extend shelf life of oxygen sensitive products. Especially effective is polybutadiene oligomer. It is not fully understood whether or not this effectiveness is because carbon to carbon double bonds (olefinic unsaturation) are present in polybutadiene oligomer. It was also disclosed that the oligomers could be functionally terminated with a chemical group capable of entering into polycondensation reactions. The functionally terminated polyolefin oligomers were then incorporated as blocks in a polycondensate. The copolycondensates, such as copolyesters and copolyamides, were extremely compatible with commonly used packaging polycondensates and as such amenable for use in packaging articles. In this application, this concept has been extended to the use of a polyether oligomer (specifically polypropylene oxide) as the oxygen scavenging moiety. There is no olefinic unsaturation what-so-ever in polypropylene oxide oligomer. While not wishing to be bound by theory, it is Applicants' belief that oxygen scavenging occurs not only at the $-\text{CH}_2-$ sites in polypropylene oxide but also at the $-\text{O}-$ ether sites.

In order to incorporate the polypropylene oxide oligomer into a packaging copolycondensate, it was first necessary to add terminal functional groups capable of entering into polycondensation to the polypropylene oxide oligomers. Subsequently it was possible to form copolycondensates, such as copolyesters and copolyamides, having polypropylene oxide oligomer segments. The weight percent of polypropylene oxide oligomer segments, the molecular weight of the polypropylene oxide oligomers, and the average diameter size of the polypropylene oxide oligomer segments had to be determined to achieve optimum compatibility, clarity and scavenging capacity as was the case for copolycondensates having polyolefin oligomer segments. These polypropylene oxide oligomer containing copolycondensates are typically deployed as at least one layer in the wall of a multi-layer packaging article.

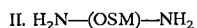
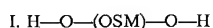
U.S. Pat. No. 5,605,996 (Chuu et al.) discloses the use of propylene oxide rubber as an oxygen scavenger but requires the presence of both olefinic unsaturation and moisture to function as an oxygen scavenger. Applicants' copolycondensates having polypropylene oxide oligomer blocks contain no olefinic unsaturation and scavenge oxygen either in the absence or presence of water (moisture) when promoted with suitable catalyst. U.S. Pat. No. 5,529,833 (Speer et al.) discloses a multi-layer oxygen scavenging structure wherein at least one layer consists essentially of an ethylenically unsaturated hydrocarbon. As noted above, applicants'

copolycondensates having polypropylene oxide oligomer blocks contain no olefinic unsaturation.

The prior related applications cited above are all directed to compositions which comprise copolymers of condensation polymers, especially polyesters and polyamides. The copolymers are active oxygen scavengers because blocks of segments comprising oxygen scavenging moieties have been implanted into the copolycondensates. In the prior related applications, Applicants have disclosed the use of polypropylene, poly(4-methyl)1-pentene and polybutadiene as oxygen scavenging moieties which are effective when included in a polycondensate. In this application, the use of polypropylene oxide oligomer has been disclosed as an oxygen scavenging moiety. While many embodiments have been disclosed involving the use of the previously disclosed oxygen scavenging copolycondensates, compatibility with package construction is optimal when the oxygen scavenging copolycondensates are used in polycondensate based packages. For example, the oxygen scavenging copolyesters are most compatible when used with adjacent layers of packaging polyester. In a similar manner, the oxygen scavenging copolyamides are most compatible when used with adjacent layers of packaging polyamide. While packaging articles based on polycondensates are very common, there still exists a wide variety of applications for packaging articles based on addition type polymers.

In several embodiments of this invention, applicants have extended the concept of incorporation of high oxygen scavenger capacity moieties into addition type polymers so as to create addition type oxygen scavenging copolymers. These oxygen scavenging addition type copolymers may be used in any suitable embodiment but are intended primarily for use in addition polymer based packaging articles such as those comprising polyolefins including polypropylene, polyethylene, and mixtures of the preceding. As was done for polycondensates, Applicants disclose the use of polyolefin oligomers, preferably polypropylene, poly(4-methyl)1-pentene, polybutadiene, and also the use of polypropylene oxide as preferred oxygen scavenging moieties which are effective scavengers when included in polyaddition polymers. Further, Applicants preferred method of preparation is by transesterification of pre-made polyaddition polymers. Some addition polymers may already have esterification reaction sites on the polymer backbone, for example those comprised of acrylic acid or acrylic acid derivatives. Of course many polyaddition polymers, such as polyolefins, have no esterification sites. In such instances, it is generally necessary to treat the addition polymer with a substance which can add the needed esterification sites to the addition polymers. A preferred class of reactants for such purposes is an unsaturated acid, its anhydride, or derivatives thereof. Maleic anhydride (or derivatives of it) is especially preferred and such a process is generally well known in the art as maleation.

For further understanding it may be useful to consider Formulas I and II below:



In Formulas I and II, OSM represents a divalent oxygen scavenging moiety such as polypropylene oxide or the other scavenging moieties recited above. In Formula I the dihydroxy functionally terminated form of OSM is shown and Formula II the diamino functionally terminated form of OSM is shown. The OSM may be singly functionalized or may be functionalized to a degree greater than two, but

double functionality is shown in Formulas I and II as one of many possible degrees of functionality. Also, other functional groups attached to the OSM are possible and suitable for the purposes of this invention, but only hydroxy and amino are shown for the sake of explanation and illustration. It will be obvious to those of ordinary skill in the art that the entities represented in Formulas I and II are capable of entering into polycondensation and/or transesterification reactions. In this invention, Applicants react species of Formulas I or II with addition polymers which have acid sites (or other suitable reaction sites) and incorporate the OSM into the addition polymer by condensation or esterification. The net result affords a simple and direct method for adding a precise amount of oxygen scavenging capacity in the form of the various OSM's recited above to an addition polymer.

Generally, the copolyaddition polymers will be comprised predominantly of polyaddition segments and have only enough OSM segments to provide the required oxygen scavenging capacity for the planned application. Predominantly, in this sense, is defined as over 50 wt % polyaddition segments in the addition type oxygen scavenging copolymers. In practice, the copolyaddition oxygen scavengers will be comprised of OSM segments in the range of 0.5 to 12 wt % of the scavenging copolymers. Preferably the OSM segments will comprise from about 2 to about 8 wt % of the copolymer, and most preferably from about 2 to about 6 wt % of the copolymer. As was the case for oxygen scavenging copolycondensates, it is desirable to use only the minimally required amount of OSM segments so that the oxygen scavenging addition copolymer has properties very similar to unmodified addition polymers especially the addition polymer from which its segments were derived. A PCT Patent Application (Ching et al.) published on Dec. 19, 1996 and designated as WO 96/40799 discloses a polyethylenic polymer having a backbone with esterification/transesterification sites located thereon and methods of esterification of said sites. The Ching et al. patent further discloses attachment (at the active sites) on the polymer of pendant groups which have a carbon atom having an attached hydrogen atom wherein said carbon atom is adjacent to a list of moieties as further recited in the Ching et al. disclosure. In practice, the Ching et al. reference ultimately discloses a composition comprising a transition metal and a modified polyethylenic polymer capable of scavenging in the range of about 40–63 cc of oxygen per gram of composition after 28 days. The oxygen scavenging copolyaddition polymers disclosed by Applicants are easily distinguished from the Ching et al. disclosure in that Applicants' copolymers are capable of scavenging about 83 cc of oxygen per gram of copolymer in 28 days under similar conditions, even in the absence of transition metal catalyst.

In another embodiment of this invention, Applicants disclose a method for adding active oxygen scavenging capacity to widely used container coating compositions. It is a common practice in the packaging industry to use very thin plastic coatings on the inside of metal (iron or aluminum) can surfaces to prevent acidic food and beverages from corrosive attack and associated contamination with ionic metals. Particularly acute is the situation for canned carbonated beverages, such as beer and soda pop, where the dissolved carbon dioxide assures a very acidic and corrosive condition. In addition to corrosion prevention, another desirable attribute for can coating is the ability to remove unwanted oxygen from the package cavity where in such oxygen was inadvertently introduced during filling of the container. In can coatings, there is little concern with regard

to oxygen which may enter the package cavity from outside since the can metal is essentially a perfect passive oxygen barrier to permeation of outside oxygen. For packaging of beer in cans, current technology is capable of placing beer in sealed cans at oxygen levels as low as about 200 PPB. Pasteurization of the beer may further reduce the oxygen level to as low as 100 PPB which remains in the can to react with and deteriorate the beer stored in the metal can. The taste aspects of beer are highly dependent upon reaction with trace amounts of oxygen. Further reduction of the amount of head space oxygen in a beer can provides the means for better tasting beer and/or longer shelf life for beer packaged in cans, hence the need for active oxygen scavengers in can coating plastics.

Some of the most commonly used can coatings are epoxy-amine-acrylate (EAA) coatings which are sprayed on to an unfilled metal cup (i.e., a can which has not yet had the top placed on it) as a water borne composition prior to a short cure of about 2 minutes at about 200° C. Later, similarly coated and cured can tops are applied to complete the package. In all instances, curing of a water borne spray is more environmentally friendly than evaporation of organic solvents from a lacquer. For coating cans intended for use with food, beverages, and comestible products in general, the advantages of working with a water borne spray coating versus and organic solvent spray (lacquer) are even more pronounced. Applicants in this invention disclose a method for incorporation of the species of Formulas I and II above into a water based can coating emulsion thereby adding oxygen scavenging capacity to can lining formed therefrom. A PCT Patent Application (Bansleben et al.) published on Sep. 12, 1997 and designated as WO 97/32925 discloses active oxygen scavenging can coatings. However, the Bansleben et al. reference discloses only the use of an oxygen scavenging "lacquer" which may be used as a coating on cans and other rigid containers. While there are other major differences, Applicants can coatings are easily distinguished from the Bansleben et al. coating in that they are formed from a water based emulsion and applied to the can as a water borne spray as opposed to a lacquer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross sectional view of a preferred oxygen scavenging bottle wall and film construction.

FIG. 2 is a graph showing the oxygen uptake of oxygen scavenging addition copolymers over a 28 day period at 60° C.

FIG. 3 is a graph showing the amount of oxygen scavenged per gram of can lining material for various can lining compositions.

FIGS. 4 is a graph showing the oxygen scavenging capacity of several block condensation copolymers of this invention.

DETAILED DESCRIPTION OF THE INVENTION

Oxygen Scavenging Container Coating Embodiments

This embodiment serves to solve the problem of how to incorporate a solid oxygen scavenging polymeric substance in a can coating in such a manner that the inclusion of the oxygen scavenger does not denigrate the viscosity/rheological characteristic of a water based emulsion. It is generally more environmentally friendly to apply plastic can coats via a water borne spray or emulsion rather than non-aqueous alternatives where the spray is in the form of a lacquer based on organic solvents which must eventually be

evaporated to form the can coating. This is even more important for the coating of cans which are destined to contain comestible products.

The use of epoxy-amine-acrylate (EAA) formulations applied as a water based spray for coating cans is already widely in use commercially. Billions of containers are coated annually with such formulations. Typical of such coating formulations are ICI/Glidden's (EAA) aqueous emulsions which routinely contain about 18% solids in the emulsions. Applicants have found that oxygen scavenging properties can be added to such a coating by directly including a small amount of the species depicted previously in Formulas I and II. Preferred for can coatings are the species of Formulas I and II when the OSM is polybutadiene oligomer or a polypropylene oxide oligomer. Especially preferred is the dihydroxy terminated polybutadiene oligomer because of its high oxygen scavenging capacity and its commercial availability.

In all instances, an objective of this invention is to use only the minimum amount of OSM necessary so that modified compositions remain similar in properties to unmodified compositions. In this embodiment, using only a small amount of OSM serves to make the modified EAA as similar as possible to the EAA absent the addition of OSM. By conducting spraying experiments using equipment similar to that which is used for can coating production runs, Applicants determined that reactive EAA dispersions having in the range of 1 to 5 wt % (with respect to the weight of the solids in the dispersion) of functionally terminated OSM were still essentially identical in physical properties to the unmodified EAA. Also addition to the EM mixture of a transition metal in the range of 10–500 PPM (calculated as metal with respect to the weight of the solids in the emulsion) to serve as a catalyst for reactions of the OSM with oxygen did not negatively affect the spray and/or cure properties of the water borne emulsion. The preferred transition metal catalyst is cobalt and especially preferred is cobalt added in the form of a cobalt carboxylate, most especially preferred is cobalt from cobalt octoate. Other spray tests were made wherein the composition further comprised 50–500 PPM (with respect to the weight of the solids in the emulsion) benzophenone (BNZ) to further enhance the rate of oxygen uptake by the OSM. Again, EAA compositions comprising (1) functionalized OSM and transition metal or (2) functionalized OSM, transition metal, and BNZ were found to spray and cure into a can lining in a manner virtually identical to the unmodified EAA when deployed in the ranges recited above.

Applicants further determined that the OSM, transition metal, and BNZ could be added directly and independently to the EAA emulsion or that the OSM, transition metal, and BNZ could be mixed together and then added to the EAA emulsion. Applicants' preferred method of preparing the formulation comprised mixing at least the OSM and the transition metal catalyst prior to mixing with the EAA emulsion. Regardless of the order in which the components of the composition were mixed or added, it was necessary to store the formulated composition in an inert environment, such as under a nitrogen blanket, in order to prevent degradation (gelling/thickening) of the final composition prior to spraying. Even when stored under nitrogen, the modified emulsions should be applied within 72 hours of formulation for best results. As was determined in the related applications, a molecular weight for the OSM in the range of about 1000–3000 produced good results and is preferred. The decomposition products of the OSM's employed in the compositions of this invention (after reaction with oxygen)

are not precisely known, nor is there any reason to believe they may be toxic. However, Applicants prefer to practice this invention by using two thinner coats of EAA emulsion to form the can coating. A first coat of EAA emulsion containing the oxygen scavenger additives (OSM, transition metal, and BNZ) is typically directly sprayed on to the can metal (usually iron or aluminum) and at least partially cured. Then a second coat of unmodified EAA emulsion is applied and cured. As has been the case in related cases, such a coating construction permits only the unmodified EAA to be in contact with the can cavity and/or its contents. In such a construction, it would be necessary for headspace oxygen to permeate through the second (inner) coating of EAA to reach the OSM and react with it. But all reaction products are isolated from the can cavity and its contents by the inner coating of EAA.

Conversely, the contents of the can cavity are isolated from the modified EAA coating.

A review of the usage conditions for a 12 oz (355 ml) beer can helps to understand some of the further-necessary considerations. Such a beer can when commercially sprayed with EAA emulsion in the form of a cup (i.e., a beer can absent the beer can lid) typically ends up with a cured coating having a weight of about 0.1 g. The can lid is added later and may be also lined with oxygen scavenging modified EAA or unmodified EAA. In the Examples section of this application, it will be shown that a cured oxygen scavenging EAA can lining formulation further comprising about 2.7 wt % OSM, 200 PPM transition metal, and 200 PPM BNZ consumes in excess of 5.0 cc of oxygen per gram at room temperature and pressure in about 70 days. In theory then, the 0.1 g of material present in the can cup lining could consume about 0.5 cc of oxygen in 70 days. Major US beer producers estimate that over 95% of their beer is in consumer hands within 60 days of bottling/canning so a 70 day shelf life would account for delivery of most of the canned beer. As previously noted, current state-of-the-art beer packaging technology is capable of filling beer cans with as little as 100 PPB of oxygen remaining in the canned beer after Pasteurization. From this it can be calculated that when filled, a 12 oz beer can having 100 PPB of oxygen contains about 0.025 cc of oxygen at room temperature and pressure. Thus in this hypothetical case, there is a 20 fold theoretical excess of oxygen scavenging capacity available. Use of EAA comprising about 5 wt % OSM could raise this to 40 fold excess, but would be reduced back to 20 fold excess if the can is lined with two layers, each of which is only half the thickness of a single layer lined can. A 20 fold theoretical oxygen scavenging capacity excess is reasonable in view of the necessity of the head space oxygen to permeate through the inner EAA layer defining the can cavity before it reaches the EAA layer having the OSM.

While the disclosure has been made largely in terms of can coatings, those skilled in the art will recognize that many container constructions could benefit from the oxygen scavenging compositions disclosed and their method of use. Application of the features of this invention to containers other than cans is envisioned by Applicants and considered to be within the scope of this invention. For example, PPG Industries produces a series of water based EAA emulsions applied as a water borne spray to form an inner lining for polyester (PET) and other plastic containers sold under the trade name BAIROCCADE®. Modification of the PPG emulsion to include OSM, transition metal, and BNZ in about the same proportions as disclosed above for can linings would yield an oxygen scavenging lining for plastic containers. Plastic bottles often have detrimental amounts of

oxygen dissolved in or adsorbed on the plastic walls of the bottle. Application of an active oxygen scavenging lining to such bottles would serve the purpose of eliminating such dissolved or adsorbed oxygen. As in the case of can lining, the application to a bottle of a modified layer followed by an inner unmodified layer which forms the surface of the package cavity would be a preferred embodiment.

Polypropylene Oxide Oligomer as an Oxygen Scavenging Moiety

In the earlier and related applications, copolycondensates, (such as copolyesters and copolyamides) having segments of oxygen scavenging moieties (OSM) consisting of polyolefin oligomers were disclosed. More specifically the polyolefin oligomers used were selected from the list consisting of polypropylene, poly(4-methyl)1-pentene and polybutadiene.

These polyolefin oligomers were first provided with functional terminal groups (usually dual functionality) capable of entering into polycondensation or transesterification reactions and subsequently included as minor percentages (based on weight) of the segments in copolycondensates. A typical weight range usage involved copolycondensates comprising 0.5 to 12 wt % polyolefin oligomer segments. Copolyesters species of this type were found to have high oxygen scavenging capacity, existed as solids at ambient temperatures in the range of 0° C. to 60° C., and had good clarity, especially when (1) used as a layer adjacent to a layer of unmodified polyester, (2) used in the presence of added transition metal as a catalyst for oxygen uptake (i.e., transition metal catalyst was added in addition to residual catalyst present, if any, from the copolymer formation), (3) subjected to a biaxial orientation of about a 2.5×4.0 stretch, (4) were made by transesterification in a reactive extruder, and (5) had pyromellitic dianhydride added during formation as a chain extending agent so as to achieve optimum molecular weight for the copolyester.

Applicants now disclose the use of polypropylene oxide oligomer as an OSM in a manner similar to what has previously been disclosed for polyolefin oligomers as briefly described above. Of course, the polypropylene oxide oligomer must first be terminally functionalized with groups capable of entering in polycondensation and/or transesterification reactions. Formulas I and II above show several options for such terminally functionalized species and reveal how such species could participate in polycondensation and/or transesterification. In Formulas I and 11, OSM could represent a divalent polypropylene oxide oligomer having a low molecular weight (MW) typically in the range of about 100 to 10,000 and preferably in the range of 1,000 to 3,000. Use of lower MW polypropylene oxide oligomer helps assure dispersion of the polypropylene oxide oligomer segments more uniformly throughout the oxygen scavenging copolycondensates. Also it has been found that lower molecular weight polyolefin oligomer leads to improved clarity in applications where clarity is of importance.

Formulas I and II show difunctionality on the polypropylene oxide oligomer but the polypropylene oxide oligomer may be singly functionalized or functionalized to a degree greater than two. Only hydroxy and amino functionalization are shown in Formulas I and II as examples that will react, but those of ordinary skill in the art will recognize that many other options are possible including carboxy, epoxy, alkoxy. The functionalization of the polypropylene oxide oligomer forms no part, per se, of this invention and such terminally functionalized species are well known in the art and commercially available. The copolycondensates of this invention

may be prepared by direct (continuous and/or batch) techniques to the degree of scavenging capacity needed by substitution of a molar equivalent amount of the species of Formula I or II, for example, for about the same molar amount of the monomer having similar terminal functionality which would normally be used to prepare the unmodified polycondensate.

Applicants also disclose the use of another class of oxygen scavenging moieties which may be designated broadly as methyl pendant aromatic compounds. Observations by Applicants indicate that $-\text{CH}_2-$ groups attached to an aromatic nucleus have commercially acceptable oxygen scavenging capacity. For this invention, methyl pendant aromatic substances are defined to be chemical compounds which are aromatic and have at least one methyl group attached to the aromatic nucleus. Examples of methyl pendant aromatic substances are toluene, the xylenes, the trimethyl benzenes, the mono, di, tri- etc. methyl naphthalenes. A requirement of such compounds is that they be attached to the copolycondensate by a linkage to one or several methyl carbon atoms regardless of their attachment, if at all, via the aromatic part of the molecule. Examples of such methyl pendant aromatic substances after dual functionalization and consistent with the species of Formula I above include the dihydroxymethyl benzenes and the dihydroxymethyl naphthalenes. These compounds may be only singly functionalized or functionalized to a degree greater than two provided more than two pendant methyl groups are available. In a similar manner the diamino counterparts of the above would satisfy the conditions for Formula II. It is significant to note that use of polypropylene oxide oligomer or methyl pendant aromatic compounds as OSM leads to the formation of copolycondensates devoid of olefinic unsaturation, provided none was present in the unmodified polycondensate.

Applicants prefer to prepare the copolycondensates by transesterification in a reactive extruder. This is achieved by melting the unmodified polycondensate in a reactive extruder and simultaneously introducing the desired weight percentage of functionalized OSM such as polypropylene oxide oligomer to the melt. Under appropriate conditions, transesterification occurs resulting in formation of a block copolycondensate having, for example, polypropylene oxide oligomer segments and polycondensate segments. Generally the transesterification is done under vacuum and optionally in the presence of a transition metal transesterification catalyst. Cobalt is the preferred catalyst, and cobalt deployed in the form of a cobalt carboxylate is especially preferred, with cobalt octoate as the most especially preferred catalyst. When used, the catalyst is deployed in the range of 10–300 PPM of the mixture in the extruder.

Only the amount of polypropylene oxide oligomer or other OSM segments needed to meet the required oxygen scavenging capacity are introduced into the copolycondensate. In all cases the copolycondensate comprises predominantly (over 50 wt % of the segments) polycondensate segments. It is desired, however, to make oxygen scavenging copolycondensate having properties as similar as possible to unmodified polycondensate especially the polycondensate from which it was derived. As such, the amount of polypropylene oxide oligomer or other OSM segments is typically held to the range of 0.5 to at 12 wt % of the copolycondensate, preferably from about 2 to about 8 wt %, and most preferably from about 2 to about 6 wt % of the copolycondensate.

The copolycondensates formed by transesterification in a reactive extruder are capable of scavenging oxygen in the solid state (below their glass transition temperatures (T_g))

and in the absence or presence of water or moisture. It is desirable to form copolycondensates which are solids at ambient filling, storage and shelf temperatures of from 0° C. to 60° C. It is frequently necessary to add a chain extending agent to the reactive extruder to form copolycondensates having T_g 's above 60° C. The chain extending agent is typically deployed in the range of 10 to 5,000 PPM with respect to the weight of the mixture in the extruder. While there may be some minor weight loss due to volatile materials, it is to be noted that the chain extending agent will be present in the resultant copolymer to about the same extent as it is present in the extruder. Aromatic anhydrides are the preferred chain extending agents and pyromellitic dianhydride is especially preferred.

Formation and use in packaging articles of many different types of oxygen scavenging copolycondensates are envisioned by applicants. A non-limiting list of polycondensates to which polypropylene oxide glycol oligomer and other OSM segments could be added includes polyesters, polyamides, polysulfones, polyols, polyethers, polyketones. The reaction conditions in the extruder for formation of the copolycondensates varies depending upon the nature of the polycondensate feed. To some extent, the temperature profile of the extruder is related to the melting temperature of the polycondensate feed. For example a temperature range of about 250° C.–280° C. is used for formation of copolyesters while a temperature range of about 280° C.–300° C. is used for copolyamides. Extruder residence times are typically in the range of about 2–5 minutes. Those of ordinary skill in the art will recognize the need to adjust and optimize extruder reaction conditions to accommodate the polycondensate feed properties. Typically the extruder reaction is conducted under vacuum to draw off volatile components. The copolycondensate formed is extruded as pellets or through a slot die and made into film. In either case, the copolycondensate is sealed in air and moisture proof containers in an inert environment, such as under a blanket of nitrogen, until needed for fabrication of packaging articles.

In one embodiment, the oxygen scavenging copolycondensates of this invention are deployed as a layer adjacent to an unmodified layer of the same polycondensate, especially the polycondensate from which the polycondensate segments in the copolycondensate were derived. In such a packaging construction, the adjacent layers have nearly identical physical properties readily lending themselves to manipulation on existing packaging equipment already in place for the unmodified polycondensate. Also, the adjacent layers tend to be self-adherent and appear to be a monolithic construction. The wide use of polyesters and polyamides in the packaging industry dictates that oxygen scavenging copolyesters and copolyamides will be the copolycondensates of choice for use in the embodiment described above.

An especially preferred type of package wall, bottle wall or film construction comprises a three layered embodiment as shown in FIG. 1. The outside of the bottle or package wall 24 is formed by a thicker layer 26 of unmodified packaging polycondensate and may be comprised of recycled material in whole or in part since it does not contact the package cavity or the packaged material. The inside of the bottle or package wall 22 which defines the package cavity is formed by a thinner layer 28 of unmodified packaging polycondensate. The middle layer 30 is comprised of the oxygen scavenging copolycondensates of this invention, i.e., those having polypropylene oxide oligomer segments, for example. The middle layer may be diluted with unmodified copolycondensate and typically further contains added transition metal catalyst, a photo-active substance, and other

routinely used additives. While the embodiment of FIG. 1 may require special extrusion equipment, it is still preferred for the following reasons: (1) it creates a structure with a relatively thick layer of exposed polycondensate which serves as a good passive barrier to oxygen from air, (2) the inner layer in contact with the packaged material is also polycondensate, typically one which has a long history of usage and acceptance for packaging of consumable materials, (3) placing the copolycondensates of this invention between two layers of unmodified polycondensates having at least reasonable passive barrier properties isolates the oxygen scavenging copolymers from direct contact with air or oxygen and preserves their oxygen scavenging ability to be applied only to oxygen which passes through the unmodified polycondensate layers, and (4) the copolycondensates and the unmodified polycondensates can be selected so as to have such similarity that they bond together when co-extruded without the need for or use of a tie layer of adhesive.

The preferred three layer embodiment described above is most easily achieved by co-extrusion of one layer of copolycondensate with the two layers of unmodified polycondensate. The copolymer is so chemically similar to the unmodified polymer that the three layers uniformly adhere to each other and form a monolithic structure upon cooling. No tie layer adhesives are required. However, in the articles of manufacture of this invention where recycling is not important, additional (and possibly diverse) layers can be incorporated to improve adhesion, improve barrier properties, reduce costs'. It may be possible to achieve the preferred three layered embodiment by techniques other than co-extrusion such as by coating with solutions or heat fusion of separate layers. Any method other than co-extrusion may have disadvantages of (1) reduction of scavenging potential by unwanted and/or inadvertent exposure of the oxygen scavenging copolymers to air or oxygen; and (2) additional processing steps. For fabrication of bottles, joining the three layers by adhesives would work against the objective of recyclability unless the adhesive was based on the copolycondensate/polycondensate. For production of films and wraps, recyclability is not nearly as important a consideration yet as it is for bottles. In fact, for films, it may even be desirable to use layers of the copolymers of this disclosure in conjunction with layers of other diverse materials such as polyethylenevinyl alcohol layers and polyolefin layers. While immediate co-extrusion of these copolymers may be the most preferred use for them, other use options are also available. For example, the copolymers could be blended as a concentrate with other polycondensates for film or bottle manufacture, or be used as an inner liner or layer in a multi-layer construction sense, for example, in packaging electronic components.

In one broad embodiment then, this invention discloses a laminar composition comprising at least one layer of a packaging material and at least one layer of an active oxygen scavenging copolycondensate comprising predominantly polycondensate segments and an active oxygen scavenging amount of OSM segments such as polypropylene oxide oligomer segments. Predominantly, as used above, means that the copolymer is at least 50 wt % polycondensate segments. Typically, the OSM segments comprise , 0.5 to , 12 wt % of the copolycondensate, preferably about 2.0 to about 8.0 wt % and most preferably about 2.0 to about 6.0 wt % of the copolymer. The layer of packaging material is typically a thermoplastic packaging material and normally one selected from the list of thermoplastic materials considered safe for use with food as listed in USA 21 CFR

§177.1010-177.2910 (revised April, 1997 edition). However, the copolycondensates of this invention may be used as active oxygen scavengers to consume head space oxygen in the form of an inner coating on cans or glass jars/bottles. In these applications, the layer of packaging material would comprise metal or glass. The preferred layer of packaging material comprises polycondensate and especially preferred are the polycondensates from which the polycondensate segments in the copolymer were derived.

However, a significant advantage of the oxygen scavenging copolycondensates of this invention is that they exist as solids at ambient temperatures and therefore can be made into films or layers independently of their potential and probable use as layer(s) in a multi-layered wall of a packaging article. As such, the copolycondensates of this invention having predominantly polycondensate segments and an oxygen scavenging amount OSM segments such as polypropylene oxide oligomer segments may be used in a packaging article as a layer in a multi-layered wall of the packaging article regardless of the nature of the other layers in the wall. Thus, the other layer(s) in the wall may be any packaging material including thermoplastics, glass, can metals (iron or aluminum), paperboard. The thermoplastic packaging materials used as layers in conjunction with the copolycondensates of this invention will typically be those as listed USA 21 CFR §177.1010-177.2910, revised April 1997 edition. Especially preferred thermoplastics are polyesters, polyamides, polyolefins, and polyethylenevinyl alcohol.

In order to optimize oxygen scavenging properties of the copolycondensates, catalysts are frequently added to enhance the uptake of oxygen by the copolycondensates. The catalysts employed are transition metals and are typically added to the copolymer during the fabrication stage of the packaging article. The transition metal is added in the range of 10-2,000 PPM with respect to the weight of the copolymer and is added in addition to remaining residual catalyst (if any) used to make the copolycondensate from direct polymerization or transesterification. For reasons not completely understood by Applicants, addition of transition metal catalyst in the range specified also seems to improve the clarity of the polycondensates, especially after biaxial orientation. The preferred transition metal catalyst is cobalt. Especially preferred is cobalt added in the form of cobalt carboxylate, and most especially preferred is cobalt added in the form of cobalt octoate.

Applicants have also discovered that employment of a photo-active substance, such as benzophenone (BNZ), further enhances the uptake of oxygen by the copolycondensates of this invention. As with the transition metal catalyst, the BNZ is typically added to the copolymer during the fabrication stage of the packaging article in an amount ranging from 10-500 PPM with respect to the weight of the copolycondensate.

In certain packaging applications, clarity of the copolycondensates of this invention and clarity of package walls comprising a layer of the copolycondensates of this invention are important considerations. Applicants have discovered that biaxial orientation of the copolycondensates of this invention improves clarity beyond what would be expected simply from diminishment of the thickness of the layer due to the stretch. The biaxial orientation of the copolycondensate is normally achieved by subjecting the copolymer to a 2.5x4.0 stretch, typical of the industry in the production of plastic bottles and packages. The oxygen scavenging copolycondensate may be first biaxially oriented and then incorporated into a packaging article or the biaxial orientation may be performed simultaneously with the other layer(s) which comprise the multi-layer package wall.

Oxygen Scavenging Addition Type Copolymers

Oxygen scavenging copolycondensation polymers disclosed above and in related applications provide for an especially advantageous embodiment wherein the modified condensation polymer (i.e., the oxygen scavenging copolycondensate having OSM's) is deployed as a layer in a packaging article wall adjacent to a layer of unmodified similar condensation polymer, especially the polycondensate from which the polycondensation segments in the copolycondensate are derived. In 1929 Carothers (W. H. Carothers, J. Am. Chem. Soc. 51,2548 (1929)) proposed a generally useful differentiation between two broad classes of polymers. One of the Carothers' classes was condensation polymers in which the molecular formula of the structural (repeating) unit or units in the polymer lack certain atoms present in the monomer or monomers from which it was formed, or to which it may be degraded by chemical means. Carothers' other class was addition polymers in which the molecular formula of the structural (repeating) unit or units in the polymer is identical with that of the monomer from which the polymer is derived. Packaging articles based on addition type polymers, such as polyolefins, especially those derived from the monomers ethylene, propylene or styrene, continue to be important in the packaging industry. Examples of such packaging include normally refrigerated plastic milk and juice bottles. As previously disclosed, the use of oxygen scavenging copolycondensates as layers in the walls of packages based on addition type polymers is a possibility but does not afford an opportunity to achieve optimal construction of extreme similarity in properties for adjacent layers in a package wall. In an effort to solve this problem, Applicants disclose oxygen scavenging copolymers comprising predominantly (over 50 wt %) polyaddition segments and an oxygen scavenging amount of OSM segments. A typical usage range will comprise copolyaddition polymers comprised of OSM segments in the range of 0.5 to 12 wt % of the copolymer. The preferred range of OSM segments is from about 2 to 8 wt % and especially preferred is from about 2 to 6 wt % of the copolymer.

The OSM's envisioned for use include polyolefin oligomers such as polypropylene, poly(4-methyl)1-pentene and polybutadiene; polypropylene oxide oligomer, and methyl pendant aromatic compounds. The preferred OSM's are polybutadiene oligomer and polypropylene oxide oligomer.

As was the case for oxygen scavenging copolycondensates, the oxygen scavenging copolyaddition polymers of this invention are preferably made by transesterification. In order for this to occur (1) it is necessary that the OSM's have terminal functionality (such as those depicted by Formulas I and II) capable of entering into condensation/transesterification reactions, and (2) there must be reaction sites (e.g., acid sites, anhydride sites, ether sites, hydroxy sites, ester sites.) On the unmodified addition polymer which is to be transformed into an oxygen scavenging copolymer. Many addition polymers have such reaction sites available and include those addition polymers comprised of monomers such as methacrylic acid, methacrylic acid, esters, of the preceding vinylalcohols. Also envisioned are oxygen scavenging copolymers whose segments are derived predominantly from ionic polyolefins such as the Surlyn® resin series available from du Pont. For addition polymers having no suitable transesterification reaction sites, it is necessary to first treat the polymer with a compatibilization agent which will add suitable reaction sites to the addition polymer. A preferred class of reactant for adding reaction sites is an unsaturated acid, its anhydride, or

substituted derivatives of the preceding. Maleic anhydride (or its derivatives) is especially preferred and such a process is well known in the art as maleation. While the availability of such sites on an addition polymer are necessary to produce the oxygen scavenging copolyaddition polymers of this invention, unmodified addition polymers having such sites are known in the art and form no part, per se, of this invention.

Addition polymers having reaction sites as described above exhibit chemical behavior similar to condensation polymers for transesterification type reactions and will react with OSM's which are functionally terminated with groups capable of entering into condensation/transesterification reactions, e.g., those depicted by Formulas I and II above. The transesterification is conducted in an extrusion reactor as was done for preparation of oxygen scavenging copolycondensates previously disclosed in this and related applications. As previously indicated, those of ordinary skill in the art will recognize the necessity of adjusting the temperature, profile of the extruder reactor to suit the needs of the unmodified addition polymer feed. Again, a major consideration in selecting reaction temperature is the melt temperature of the polymer feed which will be made into a copolymer in the extruder reactor. Surprisingly, many of the other reaction variables are maintained in the ranges similar to those used for production of copolycondensates. These similar copolymer synthesis parameters include (1) reaction with functionally terminated OSM's which are the same type and MW, (2) reactor residence times, (3) reaction under vacuum, (4) use of transition metal transesterification catalysts of the types and in the ranges previously specified for copolycondensates, (5) use of a chain extending agent to achieve the preferred molecular weight of the copolymer, (6) extrusion of the copolymer into pellets or films, and (7) storage of the copolymer pellets or films in sealed containers under nitrogen.

The method of use of the oxygen scavenging addition type copolymers is also analogous to that disclosed for oxygen scavenging copolycondensates. The oxygen scavenging addition copolymers are usually deployed in such a manner that they comprise at least one layer in a wall of a multi-layered package wall. In a series of embodiments, the oxygen scavenging copolymers are used in constructions where other layer(s) in the multi-layer package wall are comprised of other packaging materials such as glass, can metals such as aluminum or iron, cardboard, thermoplastics, (especially those as listed in USA 21 CFR §177.1010-177.2910, revised April 1997 edition), or other suitable packaging materials. For such constructions the preferred packaging materials present in the other layer(s) in the multi-layered package wall are addition polymers, and especially preferred is the addition polymer from which the addition polymer segments in the oxygen scavenger copolymer were derived. Transition metal catalysts and photoactive materials (BNZ) may optionally be added in the manner and amount as previously disclosed for the oxygen scavenging copolycondensates. The oxygen scavenging addition copolymers may optionally be subjected to biaxial orientation in the amount and manner as previously disclosed for the oxygen scavenging copolycondensates.

EXAMPLES

Examples 1-2

Examples 1 and 2 will show the method of preparation of oxygen scavenging addition type copolymers and their oxygen scavenging capacity.

Block Addition Copolymer Formation

The oxygen scavenging addition copolymers of this invention may be made on a pilot scale in a Werner and Pfleiderer ZSK-30 extruder. Example 2 and control Example 1 were processed in a Werner and Pfleiderer ZSK-30 co-rotating twin screw extruder with fully intermeshing screws having a 45:1 length to screw diameter. Pellet feed materials were metered into the first extruder section using KTRON loss-in-weight pellet feeders. The unmodified feed pellets used for these examples was ethylene methacrylic acid (EMA) polymer available under the trade name Nucrel® 599 from du Pont. Polybutadiene (PBD) oligomer diol of MW 1230 (R20LM available from Elf Atochem) is a viscous liquid and was separately conveyed using a Ruska piston style pump. The diol was injected directly onto the screws 15 diameters downstream of the EMA pellet feed at which point the polymer pellets were completely fluxed. A vacuum of at least (76.8 cm) (30 inches) was pulled on a side port of the extruder prior to processing the melt stream through a gear pump for copolymer production. The copolymer product was extruded through a 45.2 cm slot die manufactured by Extrusion Dies, Inc. (EDI) (an EDI 6 inch die onto a two roll cooling stack and then recovered as film on a constant tension winder. After recovery, the films were placed in heat sealable foil bags, purged with nitrogen, and then sealed. Extruder reactor conditions were as noted in Table 1 below.

The pressure values listed in Columns 9 and 10 of Table 1 are as indicated by the pressure gauge.

of oxygen and had consumed virtually all of the oxygen in the jar by about day 14. Since the copolymer sample jars began with about 102 cc of oxygen (20.9% of 490 cc), it can be seen that the capacity of the 4 wt % PBD copolymers is about 10 cc/g of copolymer after only 14 days. The actual scavenging capacity after 28 days could not be calculated from Example 2 since there was essentially no oxygen left in the sample jar to scavenge after day 14.

Examples 3-6

Examples 3-6 will show the method of preparation of an oxygen scavenging EAA container coating and its capacity for scavenging oxygen.

Into a glass jar was placed 100 g of ICI/Glidden's Water Reducible Spray Liner, Product Designation 640° C. 696 (18% solids) whose composition is listed in Table 2. To this aqueous emulsion was added 0.48g of Elf Atochem R45 HT polybutadienediol (PBD MW of 2800). When dried as a can coating, the dried coating comprised 2.7 wt % PBD. The mixture was stirred magnetically for one hour, then capped and sealed until it was coated onto aluminum foil with a gated blade so as to emulate a can lining. The coated foil was placed on an aluminum plate which was heated on a laboratory hot plate set at 227° C. (440° F.) for 2 minutes to obtain a baked on coating. Sixteen such foils (21 cm×5.5 cm surfaces) were fan folded, and placed into a 250 cc Mason jar equipped with a metal cap containing a rubber sampling septum. The storage temperature of 60° C. was selected in an effort to achieve accelerated testing. This composition and experiment was designated as Example 3.

TABLE 1

Preparation of Block Addition Copolymer Extruder Conditions										
Sample	Screw Speed	Torque	Polymer Rate	Additive Rate	Additive Percent (w/w)	Form of Product	Vacuum	Extruder Exit	Die	
1 EMA	60 Rpm	85%	6.8 Kg/hr (15 Lb/Hr)		NA	Film	71.1 cm Hg (28.0 in hg)	68.9 bars (1000 Psig)	53.8 bars (780 Psig)	
2 EMA Modified	123 Rpm	53%	6.9 Kg/hr (15.2 Lb/Hr)	272 g/hr (0.6 Lb/Hr)	4.0%	Film	71.1 cm Hg (28.0 in hg)	37.9 bars (550 Psig)	49.0 bars (710 Psig)	

Extruder Zone Temperatures in ° C.																
Sample	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Zone 8	Zone 9	Zone 10	Zone 11	Zone 12	Zone 13	Zone 14	Gear Pump	Die
1 EMA	120	150	175	175	175	175	175	175	175	175	175	200	200	200	200	200
2 EMA Modified	120	150	175	200	230	230	175	175	175	175	175	200	200	200	200	200

50

Oxygen Uptake of Block Addition Copolymers

Oxygen uptake was tested using film samples of 10 g. The samples were placed in 500 cc sample jars containing ordinary room air, sealed, and then held at 60° C. for the duration of the test. No transit on metal catalyst or photo-active compounds were added to the samples. Try amount of oxygen as percent in the headspace gas (air) was sampled regularly over a 28 day period via a septum on each sample jar. The oxygen present was monitored on a Mocon HS750 oxygen analyzer by withdrawal of 3 cc of gaseous aliquots at periodic intervals over the 28 day period of the test. The data from these samples are shown graphically in FIG. 2. Surprisingly, there was virtually no uptake of oxygen by the EMA polymer control of Example 1, which may be due, in part, to the absence of transition metal catalyst. After about a five day induction period, the copolymer samples having 4 wt % PBD oligomer segments showed a dramatic uptake

TABLE 2

Chemical Composition of Water Reducible Spray Liner: ICI/Glidden Paints - Product 640 C 696 (MSDS listed)			
Trade Name	Chemical Name	CAS Number	Wt. %
Dimethylamino-ethanol	Ethanol, 2-(dimethylamino)	108-01-0	1-5
Melamine Resin	1,3,5-Thiazine-2,4,6-triamine, polymer with formaldehyde, methylated	68002-20-0	1-5
N-Butanol	1-butanol	71-36-3	5-10
2-Butoxyethanol	Ethanol, 2-butoxy	111-76-2	5-10
Formaldehyde	Formaldehyde	50-00-0	0.01
Acrylic Latex	2-Propenoic acid, 2-	64112-61-4	5-10

65

TABLE 2-continued

Chemical Composition of Water Reducible Spray Liner: ICI/Glidden Paints - Product 640 C 696 (MSDS listed)			
Trade Name	Chemical Name	CAS Number	Wt. %
Epoxy Ester	methyl-, polymer with ethenylbenzene, ethyl 2-propenoate and N-((2-methylpropoxy)methyl)-2-propenamide	25068-38-6	1-5
Epoxy Acrylic Resin	Phenol, 4,4'-(1-methylethylidene)bis-, polymer with (chloromethyl)oxirane	28262-39-7	5-10
Water	2-Propenoic acid, 2-methyl-, polymer with (chloromethyl) oxirane, ethenylbenzene and 4,4'-(1-methylethylidene)bis(phenol)	7732-18-5	60-70

Another similar composition and experiment, designated as Example 4, was prepared and performed. For Example 4, 0.48 g of PBD diol was added to the 100 g of the EAA emulsion as in Example 3 to achieve the same 2.7 wt % PBD (based on 100% weight of solids in the emulsion or cured weight of can liner). Also, 200 PPM (metal) cobalt octoate and 200 PPM benzophenone (BNZ) were separately added to the EAA prior to stirring. The 200 PPM of cobalt and BNZ were calculated with respect to the weight of the solids in the EAA emulsion. As for Example 3, a total of 4.5 g of coating (which was 2.7 wt % PBD) was used in this manner to determine oxygen uptake by periodic sampling during storage at 60° C. under 0% relative humidity (ORH).

Another similar composition and experiment, designated as Example 5, was prepared and performed. The composition of Example 5 was the same as for Example 4 except that the 0.48 g PBD diol, the 200 PPM cobalt (as metal) from cobalt octoate and the 200 PPM BNZ were thoroughly mixed prior to introduction to the EAA emulsion. The 200 PPM of cobalt and BNZ were calculated with respect to the weight of the solids in the EAA emulsion. As for Example 3 and 4, a total of 4.5 g of coating (which was 2.7 wt % PBD) was used in a similar manner to determine oxygen uptake by periodic sampling during storage at 22° C. under 100% relative humidity. Obviously a temperature of 22° C. and 100% relative humidity more closely emulates the conditions inside a can of comestible product during storage as opposed 10 to 60° C. and 0% relative humidity used for Examples 3 and 4. Example 6 was the control where 4.5 g of unmodified EAA coating was prepared and tested in a manner similar to that used for Examples 3-5.

In all three test experiments (Examples 3-5) it was found necessary to maintain the modified EAA emulsion in an oxygen-free environment such as under a blanket of nitrogen. The presence of air (oxygen) caused the modified EAA emulsions to gel and would render them unsprayable in an industrial setting. Under nitrogen, the modified EAA emulsions showed no indication of increase in viscosity when used within 3 days of preparation.

The oxygen present in the headspace in the jars was monitored on a Mocon HS750 oxygen analyzer by withdrawal of 3 cc of gaseous aliquots at periodic intervals over the 85 day duration of the test period. The percent oxygen remaining in the headspace was converted, by calculation, to the amount of oxygen scavenged per gram of can liner for each of Examples 3-6. The results are displayed graphically

in FIG. 3. It is obvious from FIG. 3 that premixing of the PBD, cobalt octoate, and BNZ produces a much high oxygen scavenging capacity can liner. Applicants speculate that the premixed concentrate (Ex. 5) provides a better opportunity for intimate contact of the catalysts with the PBD than in the dilute mix (Ex. 4). The results from Example 3 having no catalyst clearly shows diminished scavenging capacity for formulations which are otherwise essentially identical.

Oxygen Scavenging Block Copolycondensates

The following examples will show the method of synthesis of oxygen scavenging copolycondensates of this invention and their ability and capacity to behave as active oxygen scavengers. These copolycondensates may be made on a pilot scale in a Werner and Pfleiderer ZSK-30 extruder. The materials were processed in a Werner and Pfleiderer ZSK-30 co-rotating twin screw extruder with fully intermeshing screws having a 45:1 length to screw diameter. Pellet feed materials were metered into the first extruder section using KTRON loss-in-weight pellet feeders. When more than one pelletized component was fed in this manner, the minor components were slaved to the primary resin feeder and all feeds ratios were maintained by the controls. Liquid components, including polypropylene oxide oligomer, were fed using either a Lewa diaphragm pump which was supplied from a heated and agitated feed vessel or a Ruska piston style pump. The OSM, and additives if any, was injected directly onto the screws 15 diameters downstream of the EMA pellet feed at which point the polymer pellets were completely fluxed. A vacuum of at least (76.9 cm) (30 inches) was pulled on a side port of the extruder prior to processing the melt stream through a gear pump for copolymer production. The copolymer product was recovered either by (1) extruding through a three hole strand die, cooling the strands on a Sandvic cooling belt, and then pelletizing or (2) extruding through a 45.2 cm slot die manufactured by Extrusion Dies, Inc. (EDI) an EDI 6 inch die) onto a two roll cooling stack and then recovered as film. After recovery, the copolymer products were placed in heat sealable foil bags, purged with nitrogen, and then sealed. The materials prepared for testing are characterized in Table 3.

HYTREL 5556, 7.5 MFR is a polyester elastomer available from du Pont. PET 7207 is polyethylene terephthalate available from Shell. R20LM PBD is a polybutadiene oligomer diol of about 1280 MW available from Elf Atochem. A-3000 is an oxygen scavenging copolyester comprising about 96 wt % PET segments and about 4 wt % PBD oligomer segments. CAPRON 8270 is polyhexamethylene-adipamide available from Allied. JEFFAMINE

TABLE 3

Material Composition of Samples				
SAMPLE NUMBER	RUN DATE	BASE RESIN	REACTIVE COMPONENT	COMMENTS
19440-1184	02/25/97	HYTREL 5556, 7.5 MFR		Neat Pellet, Control
19440-124-2	05/22/97	PET 7207, IV = 0.72		Control
19440-128-2	06/23/97	PET 7207	NEAT	Control
19440-130-2	06/26/97	PET 7207	NEAT	
19440-131-1	06/27/97	PET 7207	Elf Atochem R20-LM PBD	A-3000 Control

TABLE 3-continued

Material, Composition of Samples				
SAMPLE NUMBER	RUN DATE	BASE RESIN	REACTIVE COMPONENT	COMMENTS
19440-132-1	07/01/97	PET 7207	Elf Atochem R20-LM PBD	A-3000 Control
19440-133-2	07/02/97	CAPRON 8270, MI = 0.5-0.7	NEAT	Nylon 6 Control
19440-134-1	07/08/97	CAPRON 8270, MI = 0.5-0.7	NEAT	Nylon 6 Control
19440-136-2	07/15/97	PET 7207	NEAT	Control
19440-138-1	07/16/97	PET 7207	JEFFAMINE D-2000	-14.7% JEFFAMIN (NMR)
19440-139-1	07/17/97	PET 7207	JEFFAMINE D-2000/COBALT	-2.0% JEFF. (NMR), -250 PPM COB.
19440-140-1	07/17/97	CAPRON 8270, MI = 0.5-0.7	JEFFAMINE D-2000/COBALT	-4% JEFF., -500 PPM COB.
19440-140-2	07/17/97	CAPRON 8270, MI = 0.5-0.7	JEFFAMINE D-2000/COBALT	4% JEFF., -500 PPM COB.
19440-142-1	09/09/97	PET 7207	Elf Atochem R20-LM PBD	First Ruska pump sample
19440-143-1	09/11/97	PET 7207	Dow P-1200	
19440-144-1	05/15/97	PET 7207	Dow P-1200/ Cobalt Octoate	500 ppm cobalt octoate
19440-146-1	09/18/97	PET 7207	JEFFAMINE D-2000/COBALT	500 ppm cobalt octoate
19440-147-1	09/19/97	CAPRON 8270, MI = 0.5-0.7	NEAT	
19440-147-2	09/19/97	CAPRON 8270, MI = 0.5-0.7	JEFFAMINE D-2000/COBALT	500 ppm cobalt octoate
19440-148-1	09/25/97	PET 7207	25:75, DOW P-1200/EA PBD	
19440-149-1	09/25/97	PET 7207	25:75 DOW/ PBD + CAT + BENZO	200 ppm cobalt; 100 ppm benzo-phenone
19440-150-1	09/26/97	PET 7207	50:50, bow P-1200/EA PBD	
19440-151-1	09/26/97	PET 7207	50:50 DOW/ PBD +CAT + BENZO	200 ppm cobalt; 100 ppm benzo-phenone
19440-154-1	10/01/97	PEBAX 5533	NEAT	
19440-159-1	10/06/97	CAPRON 8270, MI = 0.5-0.7	NEAT	
19440-160-1	10/06/97	CAPRON 8270, MI = 0.5-0.7	Dow P-1200	
19440-161-1	10/07/97	CAPRON 8270, MI = 0.5-0.7	Dow P-1200 + cobalt octoate	500 ppm cobalt octoate

D2000 is a diamino terminated polypropylene oxide oligomer of about 2000 MW available from Huntsman. P1200 is a dihydroxy terminated polypropylene oxide oligomer of about MW 1200 available from Dow. BENZO is benzophenone. PEBAX 5533 is a polyamide elastomer available from Elf Atochem.

The samples of Table 3 were tested for oxygen scavenging capacity by the same technique used for Examples 1-2. Ten grams of each of the samples from Table 3 were placed in 500 ml glass jars, and then monitored for oxygen content of

the air in the jar over a 28 day period. The jars were held at 60° C. and 0% relative humidity. All of the copolycondensates of Table 3 showed substantial oxygen scavenging capacity, especially when enhanced by the addition of cobalt and/or benzophenone. FIG. 4 graphically shows the oxygen uptake results obtained for some of the PET block copolymers of Table 3.

The examples described above are intended to be illustrative of the many numerous embodiments for the oxygen scavenging compositions disclosed in this application. Those of ordinary skill in the art will recognize that variations in these compositions, including the use of various additives and additive packages, are encompassed by this disclosure and are within the scope of the invention.

We claim:

1. An oxygen barrier laminar composition comprising a layer of packaging material and a layer of active oxygen scavenging copolycondensate comprising predominantly polycondensate segments and a minor amount of oxygen scavenging moiety segments; and wherein said copolycondensate (A) has a glass transition temperature above 60° C. and scavenges oxygen in its solid state at ambient temperatures in the range of 0-60° C. and (B) is devoid of ethylenic unsaturation.

2. The laminar composition of claim 1 wherein the packaging material is a thermoplastic resin.

3. The laminar composition of claim 1 wherein the packaging material is a polycondensate.

4. The laminar composition of claim 3 wherein the polycondensate is selected from the group consisting of polyamide and polyester.

5. The laminar composition of claim 1 wherein the oxygen scavenging segments of the copolycondensate comprises from 0.5 to 12 wt % of the copolymer.

6. The laminar composition of claim 1 wherein the oxygen scavenging moiety segments are selected from the group consisting of polypropylene, poly(4-methyl)1-pentene, polypropylene oxide oligomer, methyl pendant aromatic compounds, and mixtures of the preceding.

7. A multi-layered wall packaging article having disposed within the package wall a laminar composition comprising a layer of packaging material and a layer of active oxygen scavenging copolycondensate comprising predominantly polycondensate segments and a minor amount of oxygen scavenging moiety segments; and wherein said copolycondensate (A) has a glass transition temperature above about 60° C. and scavenges oxygen in its solid state at ambient temperatures in the range of 0-60° C. and (B) is devoid of ethylenic unsaturation.

8. A method of extending the useful shelf life of an oxygen sensitive substance which comprises packaging said oxygen sensitive substance in a multi-layered wall packaging article having disposed within the package wall a laminar composition comprising a layer of packaging material and a layer of active oxygen scavenging copolycondensate comprising predominantly polycondensate segments and a minor amount of oxygen scavenging moiety segments; and wherein said copolycondensate (A) has a glass transition temperature above about 60° C. and scavenges oxygen in its solid state at ambient temperatures in the range of 0-60° C. and (B) is devoid of ethylenic unsaturation.

9. An oxygen scavenging composition comprising (A) a copolycondensate which is devoid of ethylenic unsaturation comprising (1) predominantly polycondensate segments, (2) a minor amount of oxygen scavenging moiety segments, and (3) 10-5,000 PPM pyromellitic dianhydride with respect to the weight of the copolycondensate, and (B) a transition

metal catalyst which has been added to the extent of 10–2000 PPM with respect to the weight of the copolycondensate and is added in addition to any residual transition metal which may be present from formation of the copolycondensate.

10. The oxygen scavenging composition of claim 9 wherein the transition metal catalyst is cobalt.

11. The oxygen scavenging composition of claim 10 wherein the source of cobalt is cobalt octoate.

12. The oxygen scavenging composition of claim 9 wherein the oxygen scavenging moiety segment is selected from the group consisting of polypropylene, poly(4-methyl) 1-pentene, polypropylene oxide oligomer, methyl pendant aromatic compounds, and mixtures of the preceding.

13. An oxygen scavenging composition comprising (A) a copolycondensate which is devoid of ethylenic unsaturation comprising predominantly polycondensate segments and an oxygen scavenging amount of oxygen scavenging moiety segments, (B) a transition metal catalyst which has been added to the extent of 10–2000 PPM with respect to the weight of the copolycondensate and is added in addition to any residual transition metal which may be present from formation of the copolycondensate, and (C) benzophenone in the range of 10–500 PPM with respect to the weight of the copolycondensate.

14. The oxygen scavenging composition of claim 13 wherein the oxygen scavenging moiety segment is selected from the group consisting of polypropylene, poly(4-methyl) 1-pentene, polypropylene oxide oligomer, methyl pendant aromatic compounds, and mixtures of the preceding.

15. The oxygen scavenging composition of claim 13 wherein the copolycondensate is further subjected to biaxial orientation comprising a stretch of about 2.5×4.0 to improve clarity.

16. A water based epoxy-amine-acrylate emulsion capable of forming a can coating via a water borne spray further comprising from 1 to 5% functionalized polybutadiene oligomer with respect to the weight of the solids in the emulsion and 10–500 PPM transition metal catalyst calculated as metal with respect to the weight of the solids in the emulsion.

17. The emulsion of claim 16 further comprising 50–500 PPM benzophenone with respect to the weight of the solids in the emulsion.

18. An oxygen scavenging container lining formed from the application of a water borne spray of the oligomer and catalyst containing emulsion of claim 16.

19. An oxygen barrier laminar composition comprising a layer of packaging material and a layer of active oxygen scavenging addition copolymer comprising predominantly polyaddition segments and an a minor amount of oxygen scavenging moiety segments; and further comprising transition metal catalyst which has been added to the extent of about 10–2000 PPM with respect to the weight of the addition copolymer and is added in addition to any residual transition metal which may be present from formation of the copolymer.

20. The laminar composition of claim 19 wherein benzophenone has been added to the copolymer in the range of 10–500 PPM with respect to the weight of the copolymer.

21. The laminar composition of claim 19 wherein polyaddition segments of the copolymer are derived from monomers selected from the list consisting of acrylic acid, methacrylic acid, esters of the preceding, ethylene, propylene, vinyl alcohol, and styrene.

22. The laminar composition of claim 19 wherein oxygen scavenging moiety segments comprise from 0.5 to 12 wt % of the copolymer.

23. The laminar composition of claim 19 wherein the oxygen scavenging moiety segment is selected from the group consisting of polypropylene, poly(4-methyl)1-pentene, polybutadiene, polypropylene oxide oligomer, methyl pendant aromatic compounds, and mixtures of the preceding.

24. The laminar composition of claim 19 wherein the packaging material is an addition polymer.

25. The laminar composition of claim 24 wherein the oxygen scavenging copolymer comprises addition segments derived from the packaging material addition polymer.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,346,308 B1
DATED : February 12, 2002
INVENTOR(S) : Paul J. Cahill et al.

Page 1 of 2

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 4,

Line 13, "into modern packaging articles" should read -- into modern packaging articles --

Column 8,

Line 31, "to the EM mixture of" should read -- to the EAA mixture of --

Column 9,

Line 32, "the 0.1 9 of material" should read -- the 0.1 g of material --

Column 10,

Line 47, "In Formulas I and 11," should read -- In Formulas I and II, --

Column 15,

Line 54, "ester sites.) On the unmodified" should read -- ester sites) on the unmodified --

Lines 58-59, "such as methacrylic acid, methacrylic acid," should read -- such as acrylic acid, methacrylic acid, --

Column 17,

Line 55, "No transit on metal catalyst" should read -- No transition metal catalyst --

Line 56, "the samples. Try amount of" should read -- the samples. The amount of --

Column 19,

Line 49, "opposed 10 to 60°C and" should read -- opposed to 60°C and --

Column 20,

Line 60, Table 3, "19440-1184 02/25197" should read -- 19440-118-4 02/25/97 --

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,346,308 B1
DATED : February 12, 2002
INVENTOR(S) : Paul J. Cahill et al.

Page 2 of 2

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 21,

Line 16, Table 3, "- 14.7%" should read -- ~ 14.7% --

Lines 18 and 19, Table 3, "-2.0% JEFF. (NMR), -250" should read
-- ~2.0% JEFF. (NMR), ~250 --

Lines 21 and 22, Table 3, "-4% JEFF., -500" should read
-- ~4% JEFF., ~500 --

Lines 23 and 24, Table 3, "-4% JEFF., -500" should read
-- ~4% JEFF., ~500 --

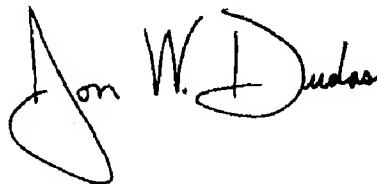
Line 43, Table 3, "PET 7207 50:50, bow P-" should read -- PET 7207 50:50, DOW P- --

Column 22,

Line 61, "devoid of ethylepic unsaturation" should read -- devoid of ethylenic unsaturation --

Signed and Sealed this

Sixth Day of April, 2004

A handwritten signature in black ink, reading "Jon W. Dudas". The signature is stylized, with a large, looped initial "J" and a cursive "Dudas".

JON W. DUDAS
Acting Director of the United States Patent and Trademark Office